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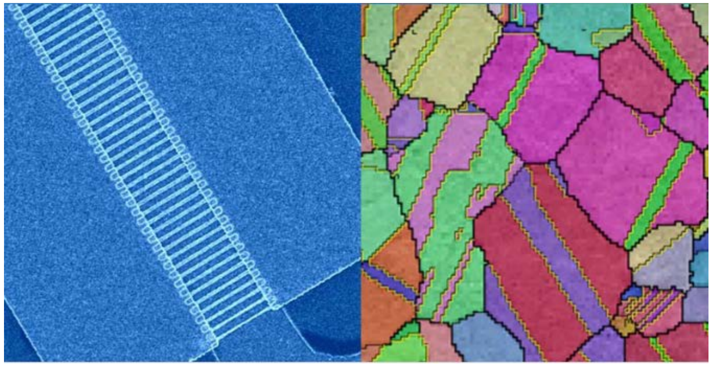
Touching the Nanoworld.
Various Ways for Surface Characterization at Nanoscale by means of AFM

Workshop on Nanomaterials Characterization.
Purdue University, Discovery Park. March, 22nd 2018

Dr. Stanislav Leesment, Senior Application Scientist
NT-MDT Spectrum Instruments



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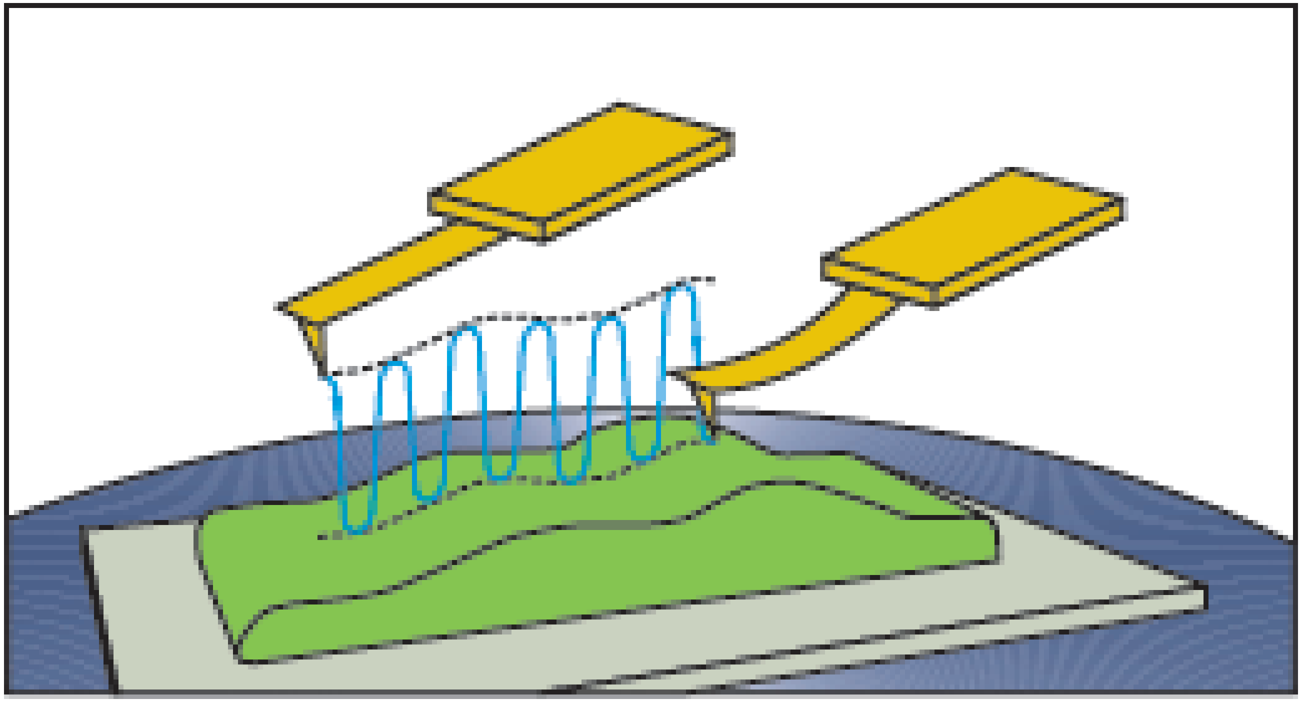
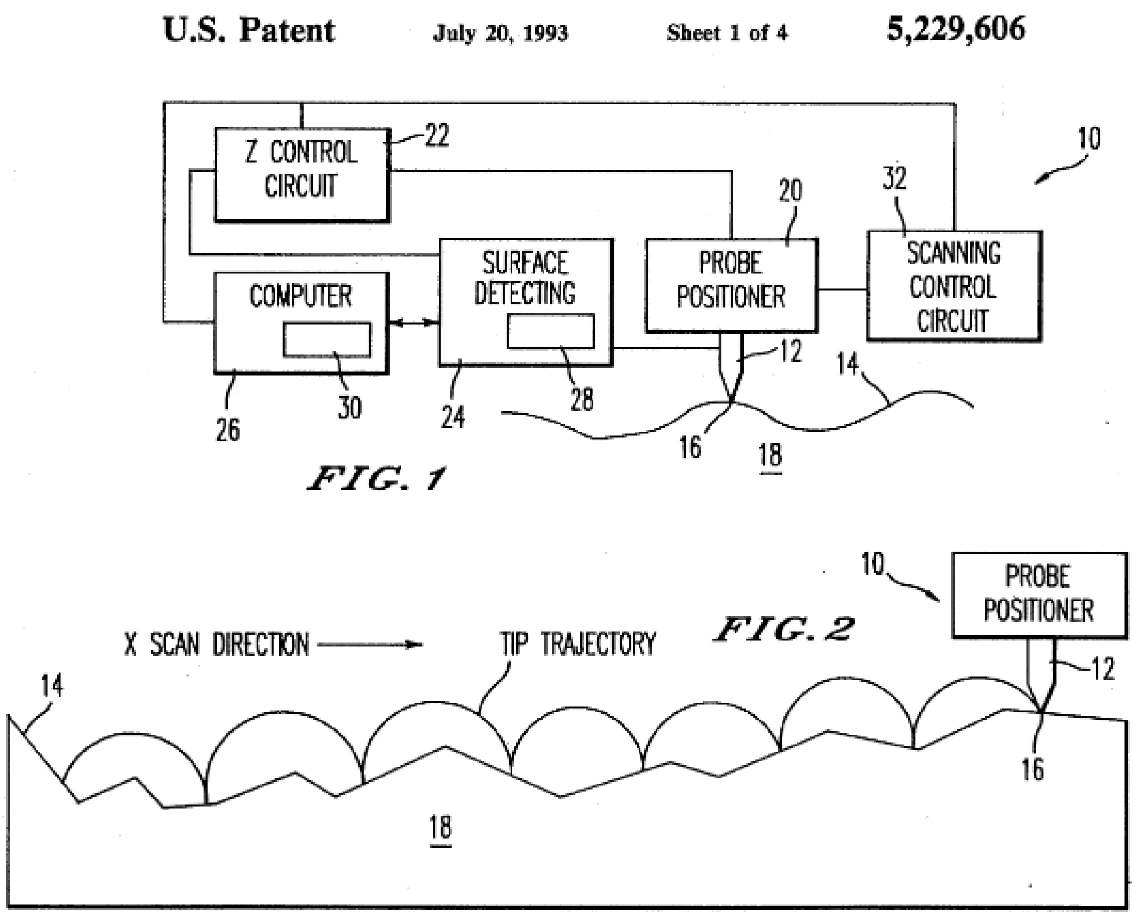
Non-Resonant HybriD™ Force Microscopy



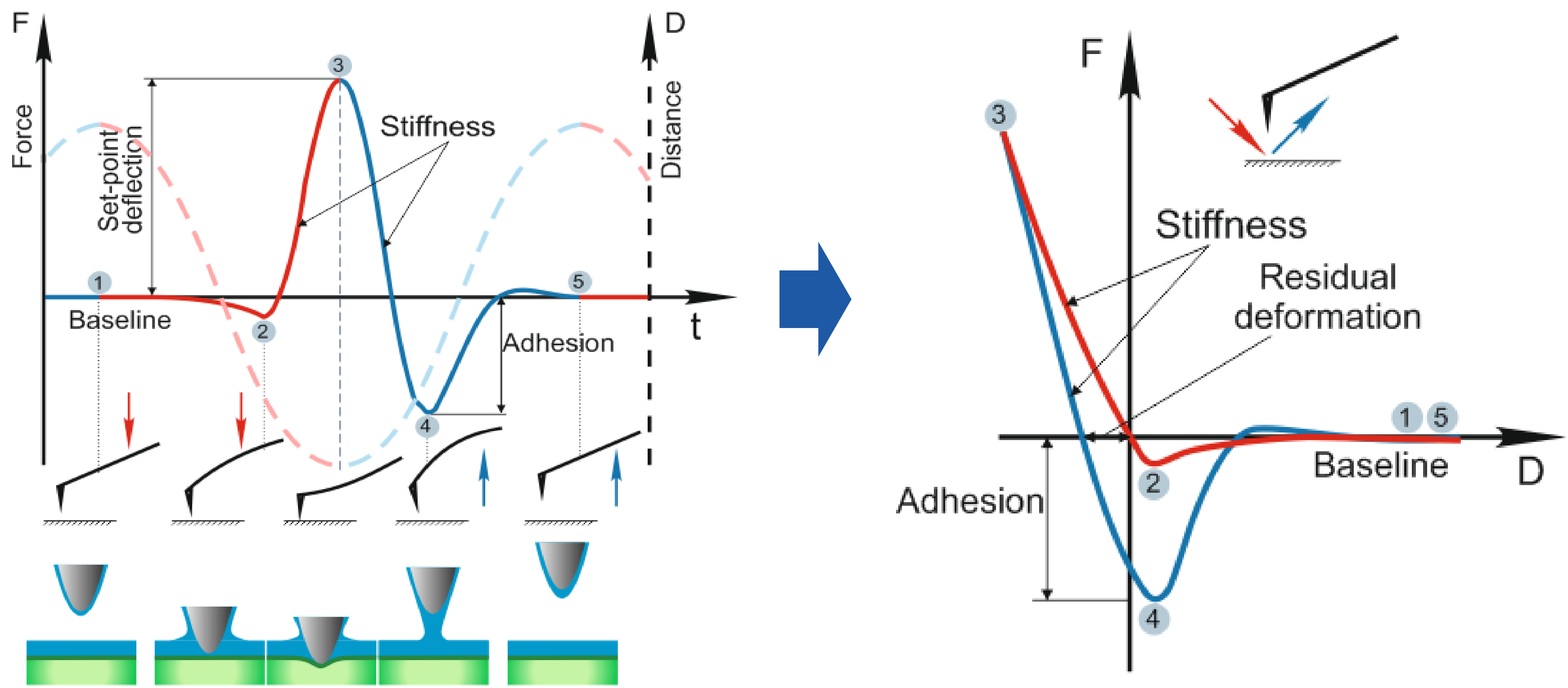
History: Jumping mode AFM



Patent US 5229606 “Jumping probe microscope”
Applied in 1989 by Virgil B. Elings, John A. Gurley

HybriD Mode working principle

HybriD mode (HD mode) – scanning technique based on fast force-distance curves measurements with real-time processing of the tip response.



HybriD mode working principle

S. Magonov, S. Belikov, J. D. Alexander, C. G. Wall, S. Leesment, and V. Bykov, "Scanning probe based apparatus and methods for low-force profiling of sample surfaces and detection and mapping of local mechanical and electromagnetic properties in non-resonant oscillatory mode," US9110092B1.

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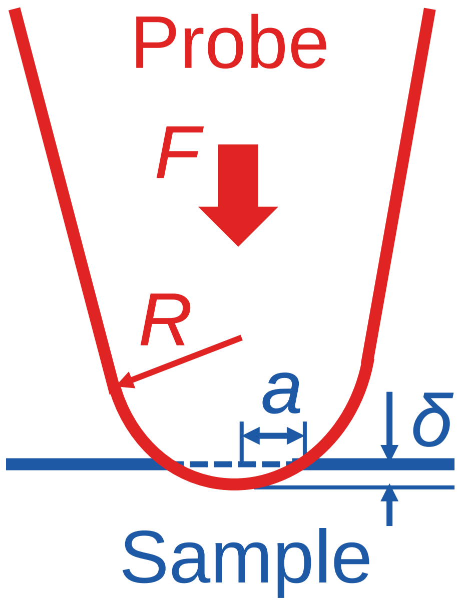
HD QNM

Quantitative nanomechanical measurements

Most used models of contact mechanics

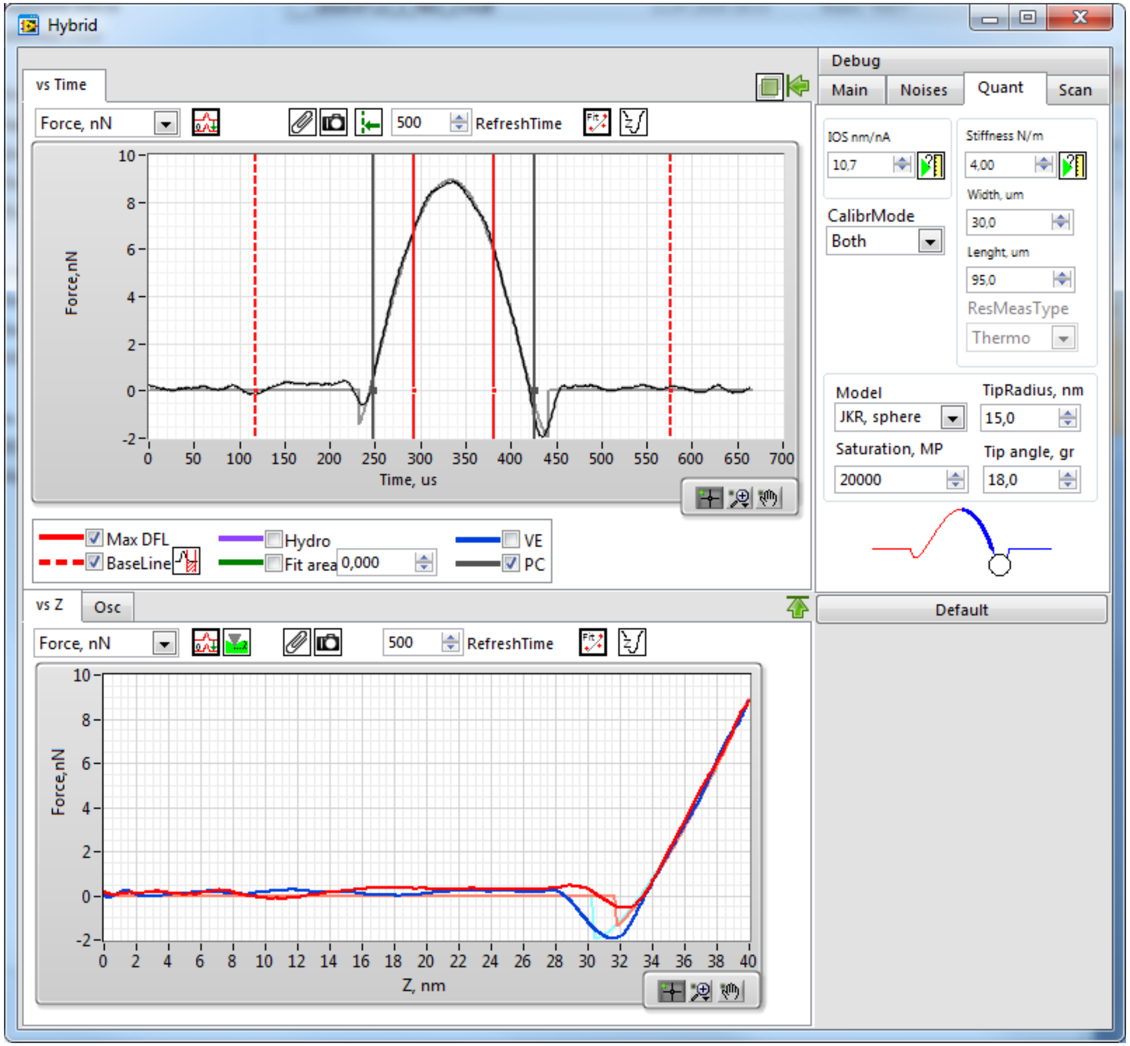


Tip-sample interaction model

Model	Approximation
Hertz model	• Large tip radius (a/R<<1) • No adhesive and capillary forces
Derjagin-Muller-Toropov model (DMT)	• Sharp tip (a≈R) • Low adhesive and capillary forces • Stiff samples
Johnson-Kendall-Roberts model (JKR)	• Large tip radius (a/R<<1) • High adhesion

Quantitative nanomechanical measurements

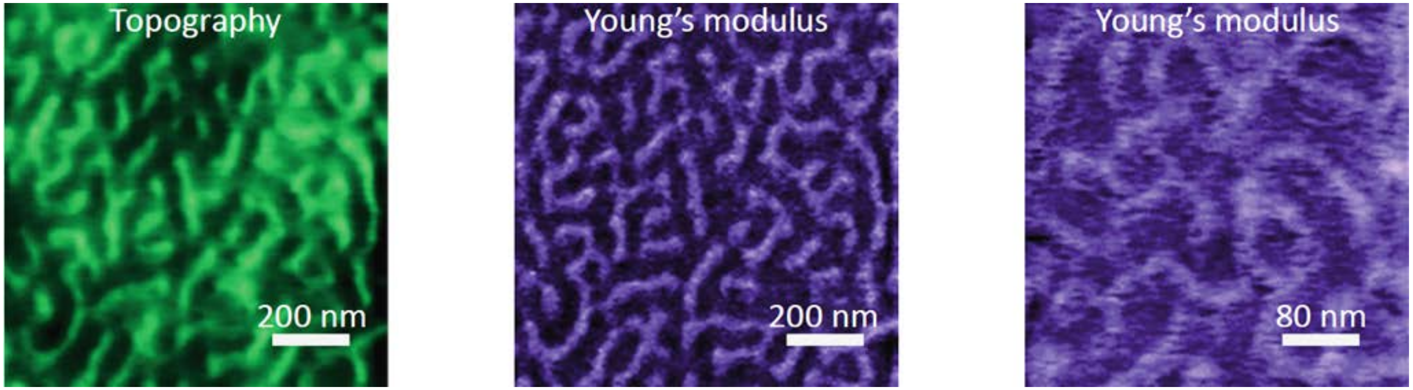
Real-time approximation of the force curves



HybriD mode software

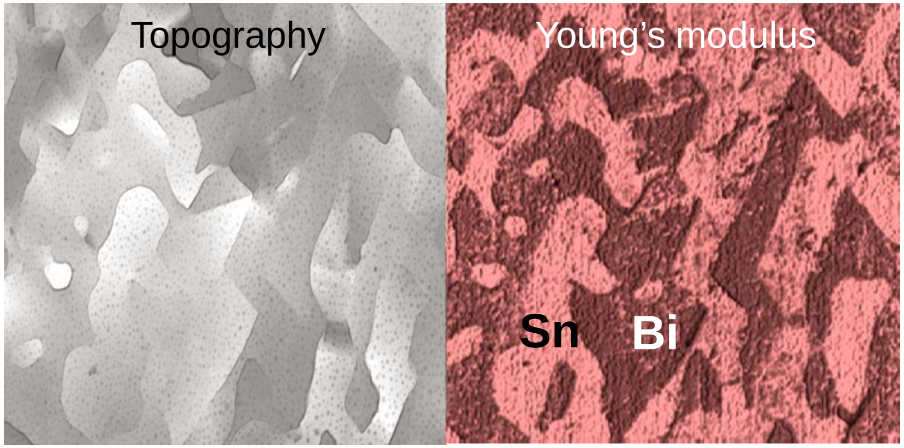
Quantitative nanomechanical measurements

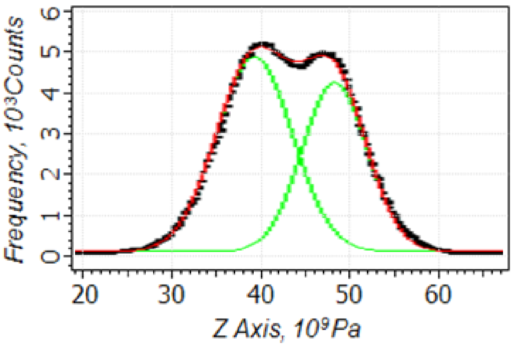
Ultimate spatial resolution



HD QNM study of PS-b-PMMA. Right image demonstrates around 10 nm spatial resolution.

Braking the force limit



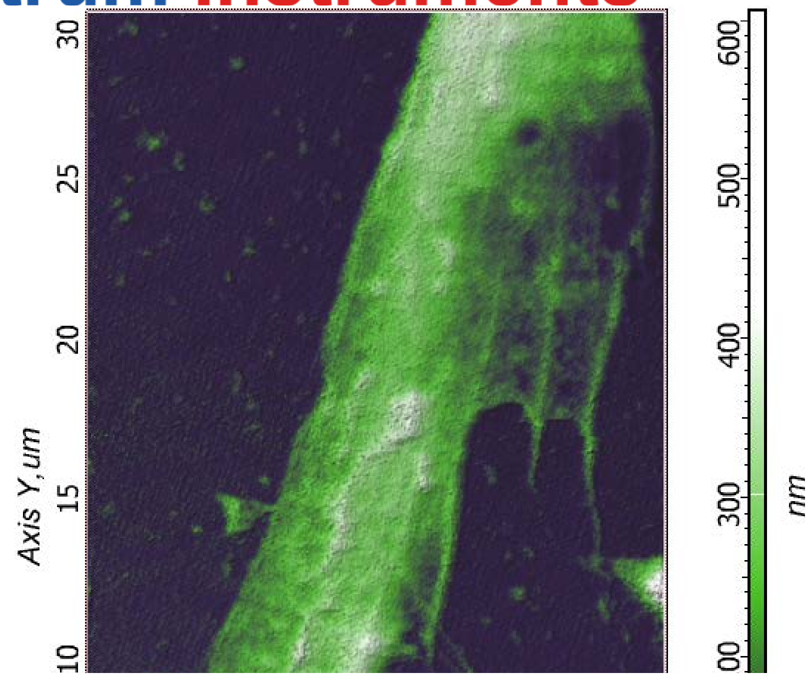


Young's Modulus:
Si: 70 GPa
Tin: 50 GPa
Bismuth: 32 GPa

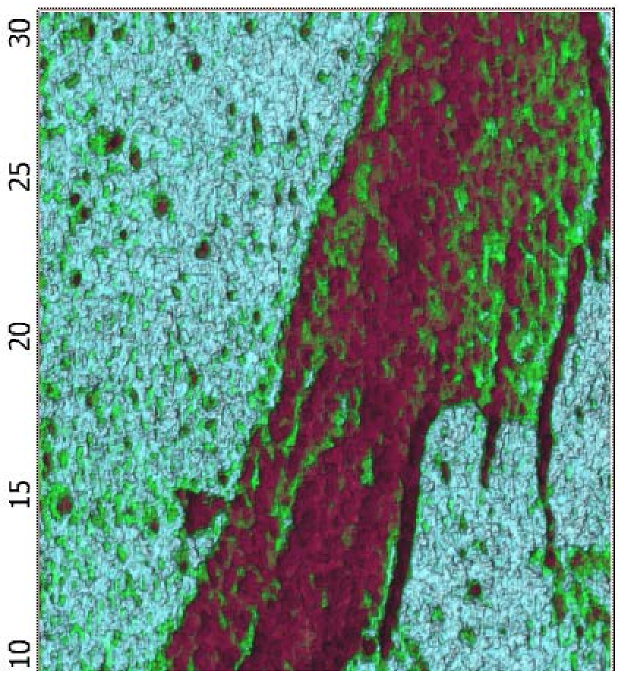
HD QNM study of Tin-Bismuth alloy. Scan size: 10×10 µm.

How **Soft** we can go?

Topography



Modulus Map



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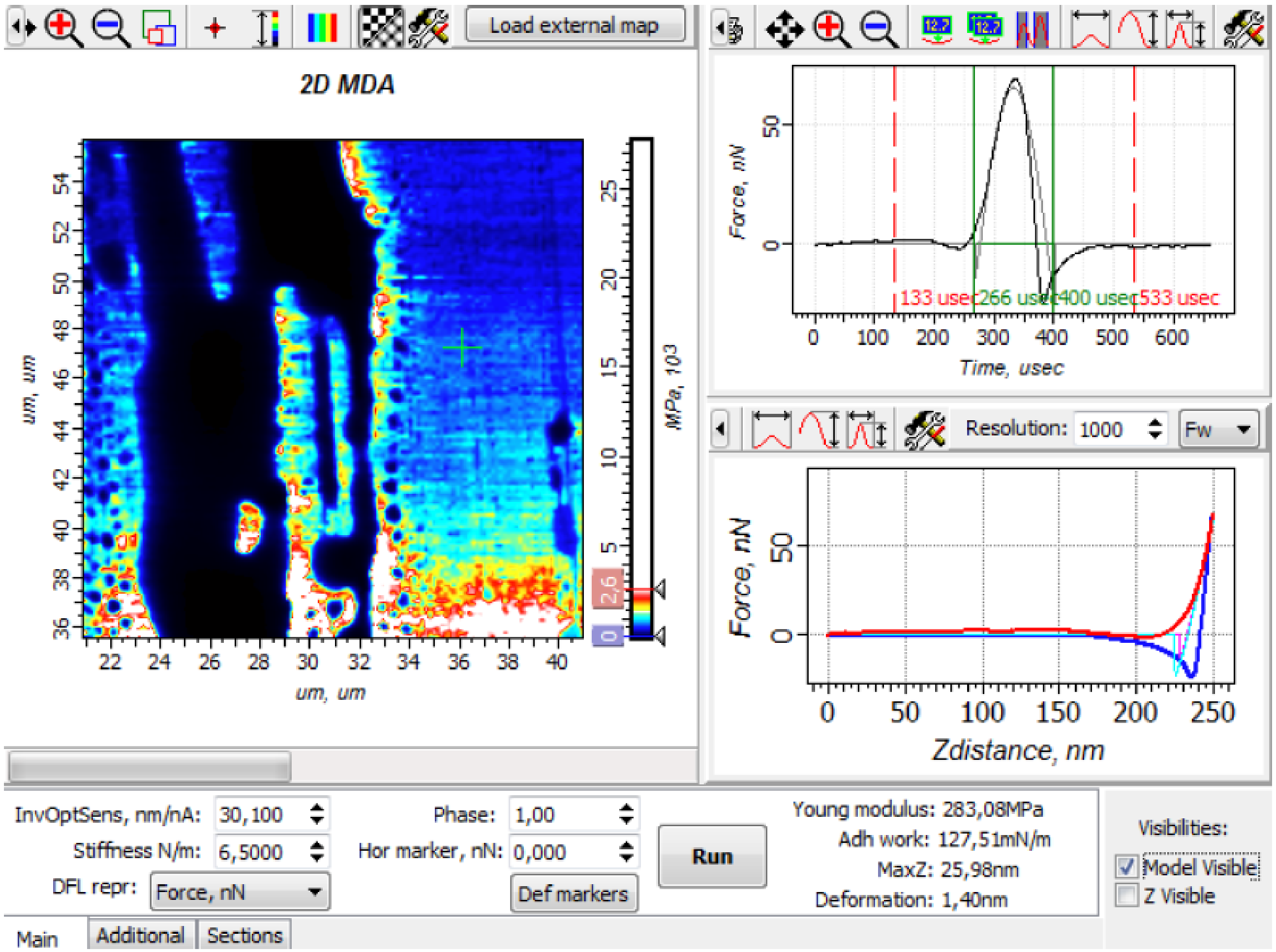
QNM Data Analysis



✓**Processing:**
Online и Post-processing

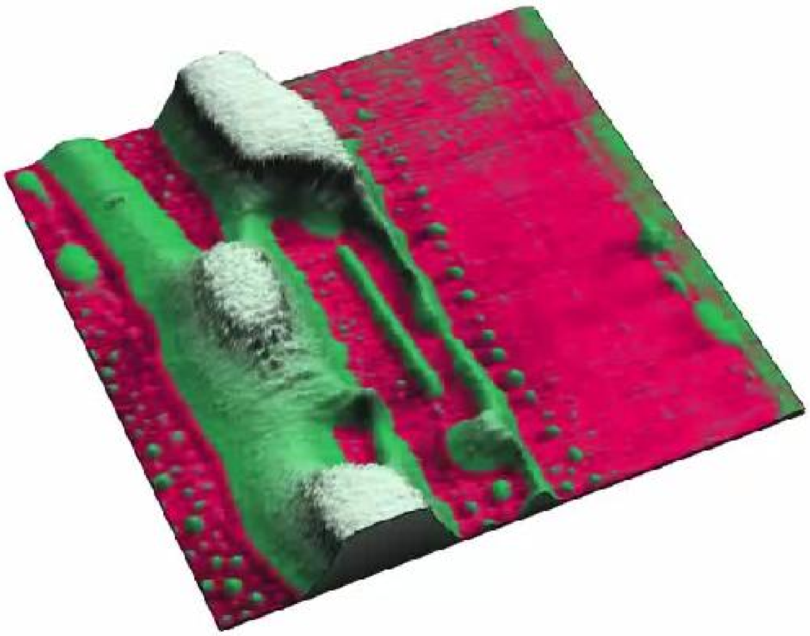
✓**Models:**
- Hertz
- DMT
- JKR

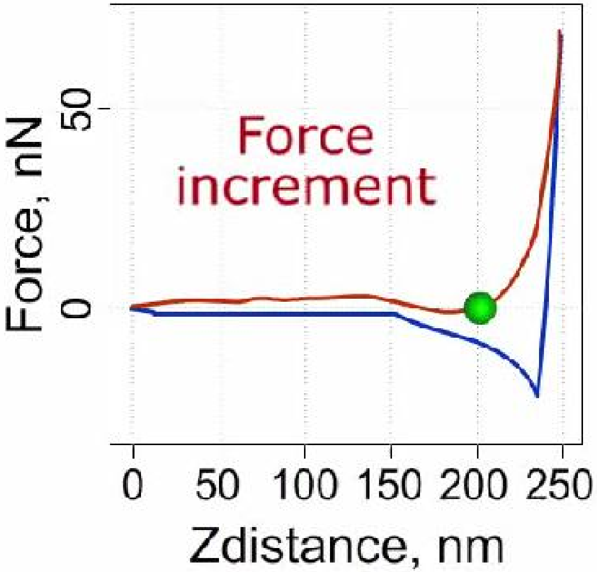
✓**Arrays:**
Up to 1000x1000 Force Curves

✓**Sections**

Isodynamic Force Spectroscopy

ισος – “Equal, ”δύναμις – “Force”





Isodynamic Force Spectroscopy

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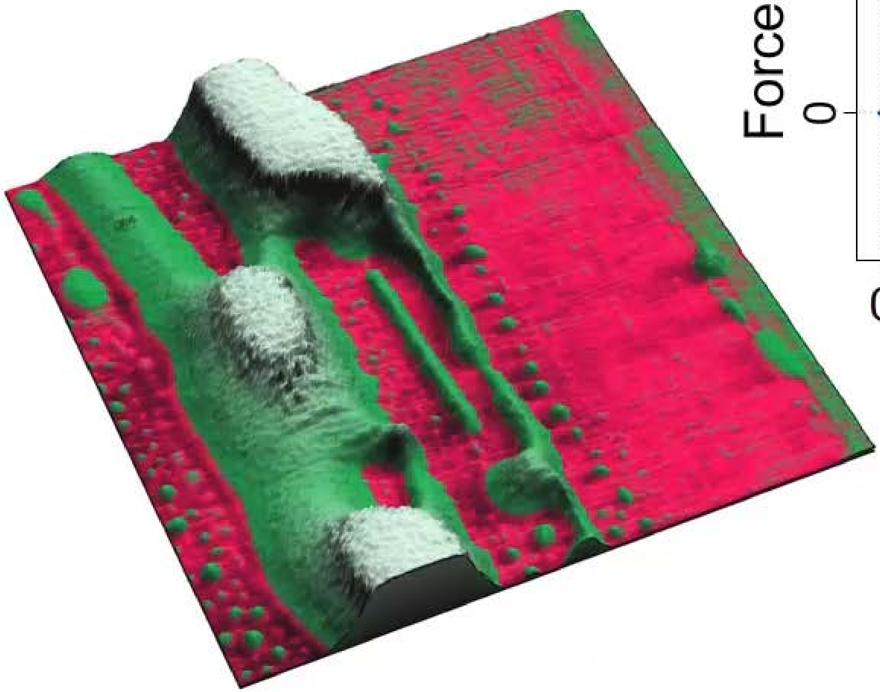
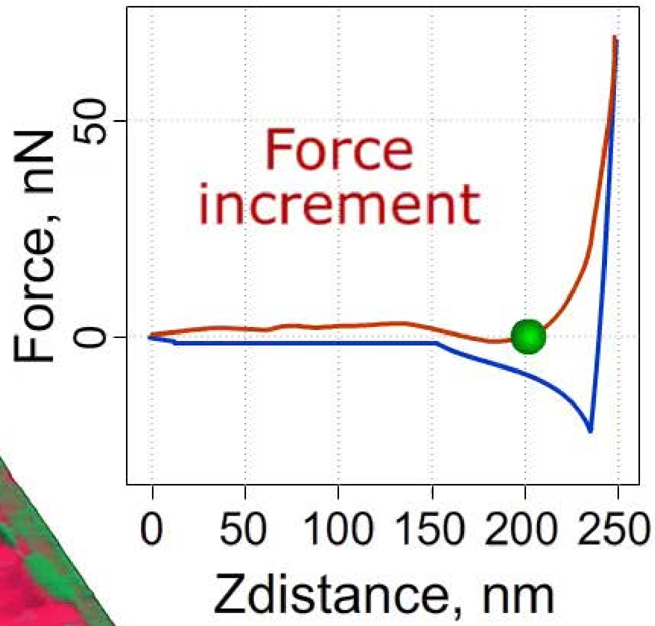
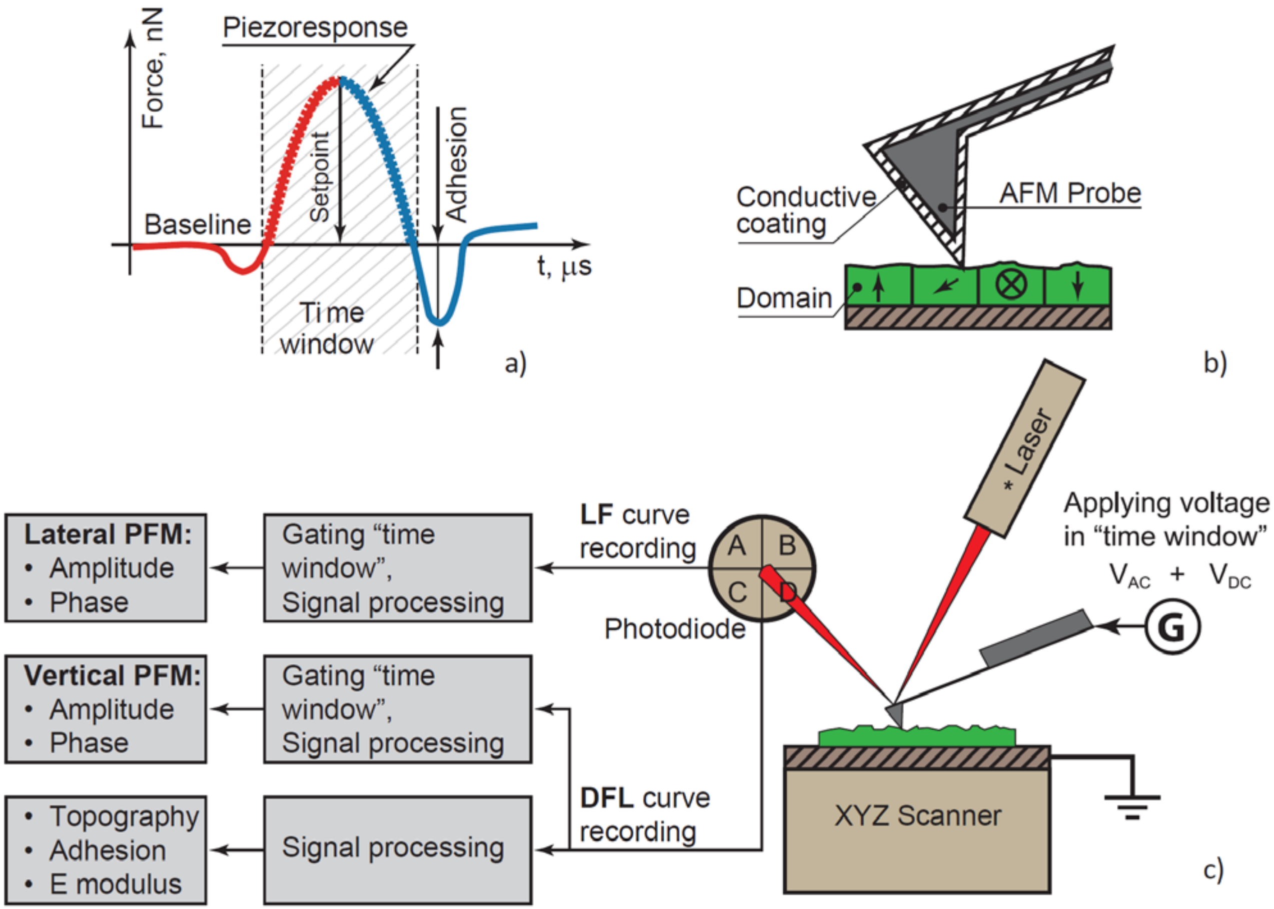




HybriD Piezoresponse Force Microscopy

HybriD Piezoresponse Force Microscopy

In HD PFM an AC voltage is applied to the conductive coating of the AFM cantilever when the tip comes in contact with the sample during each fast force spectroscopy cycle.



HD PFM working principle: a) an idealized temporal deflection curve during an oscillatory cycle, b) tip-sample interaction in “time window”, c) measurement scheme

Key advantages of HD PFM compared to the contact mode PFM:

1. **The ability of piezoresponse study of soft, loose and fragile samples**: since the AFM tip retracts from the surface in each scanning point, the lateral tip-sample interaction force is significantly reduced in comparison to the conventional contact PFM technique.

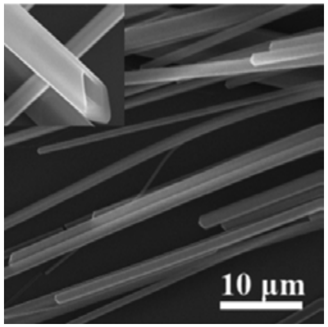
2. **Simultaneous Quantitative Nanomechanical measurements**

3. **Simultaneous** double-pass resonant electrostatic measurements: **Kelvin Probe Microscopy** or **Electrostatic Force Microscopy.**

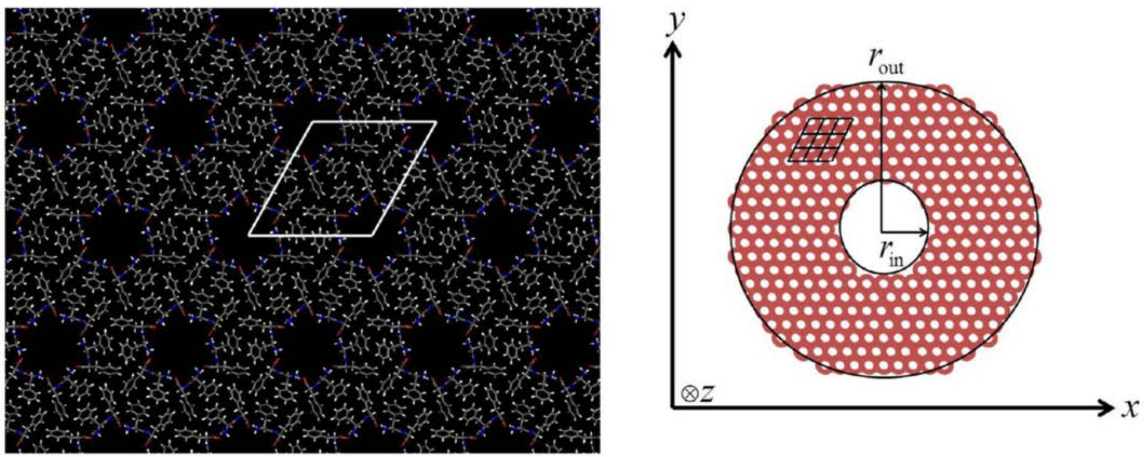
4. Automatic compensation of the thermal drift of the AFM probe at each scanning point for the **real-time PFM studies under varying temperature.**

HybriD Piezoresponse Force Microscopy

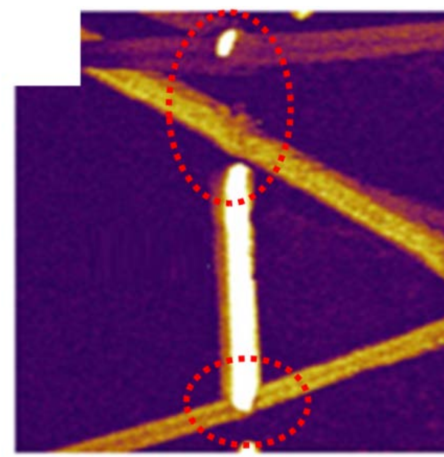
Motivation for the development: diphenylalanine peptide nanotubes



d_{15} = 60 pm/V[1]
E modulus = 19 32 GPa



Molecular structure of diphenylalanine peptide nanotubes[1]

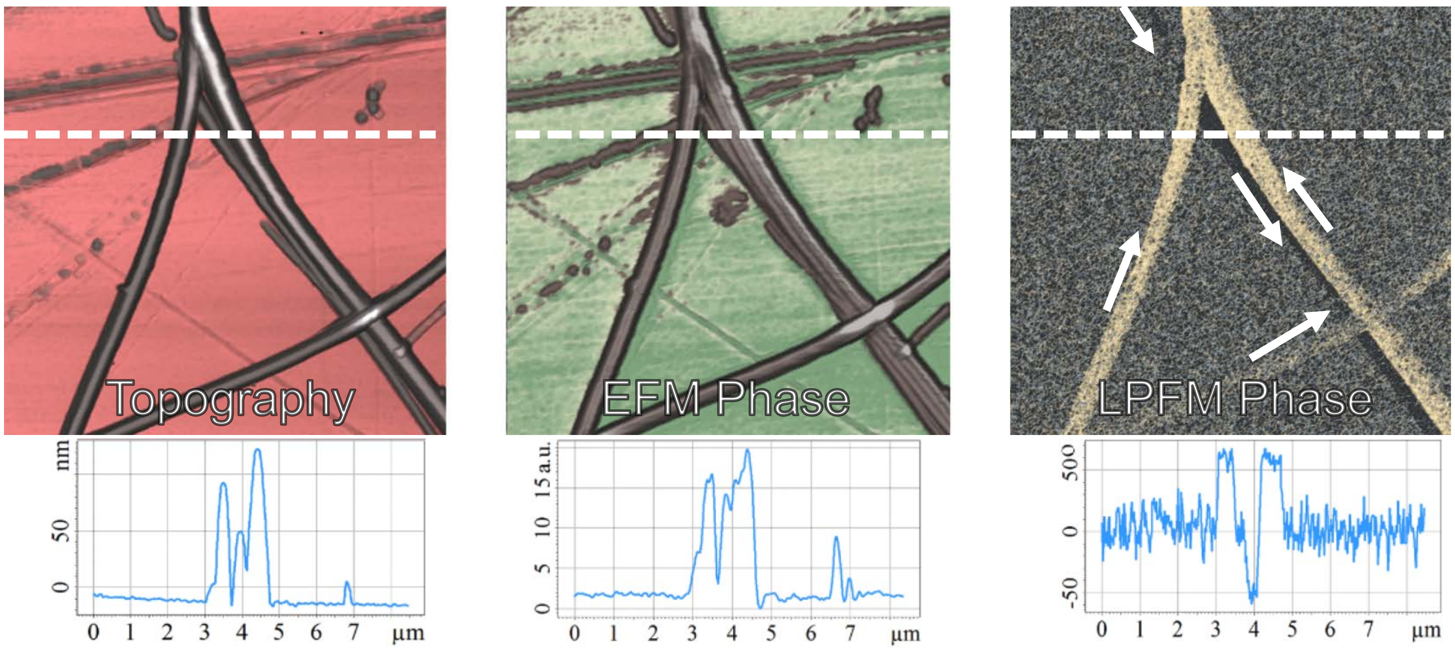


Contact PFM image[2]

[1]Kholkin, A., Amdursky, N., Bdikin, I., Gazit, E., & Rosenman, G. (2010) ACS nano, 4(2), 610-614.
[2]Ivanov, M., Kopyl, S., Tofail, S. A., Ryan, K., Rodriguez, B. J., Shur, V. Y., & Kholkin, A. L. (2016) In Electrically Active Materials for Medical Devices (pp. 149-166).

HybriD Piezoresponse Force Microscopy

For the first time HD PFM mode allowed non-destructive piezoresponse study of diphenylalanine peptide nanotubes – a very prospective material for biomedical applications.



Non-destructive electromechanical study of diphenylalanine peptide nanotubes. Scan size: 8 8 µm, nanotubes diameter: 30 150 nm[1]. Sample courtesy: Dr. A. Kholkin, University of Aviero

[1] A. Kalinin, V. Atepalikhin, O. Pakhomov, A. Kholkin, A. Tselev. An Atomic Force Microscopy Mode for Nondestructive Electromechanical Studies and its Application to Diphenylalanine Peptide Nanotubes. To be published in Ultramicroscopy

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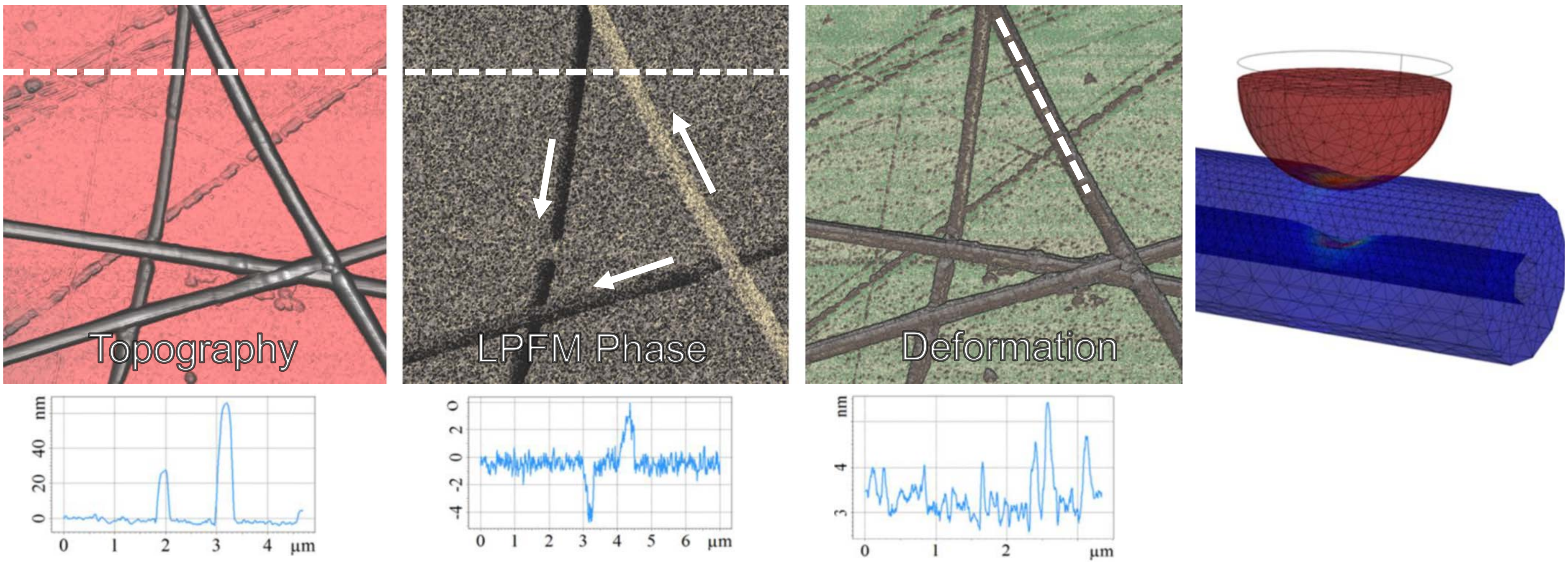

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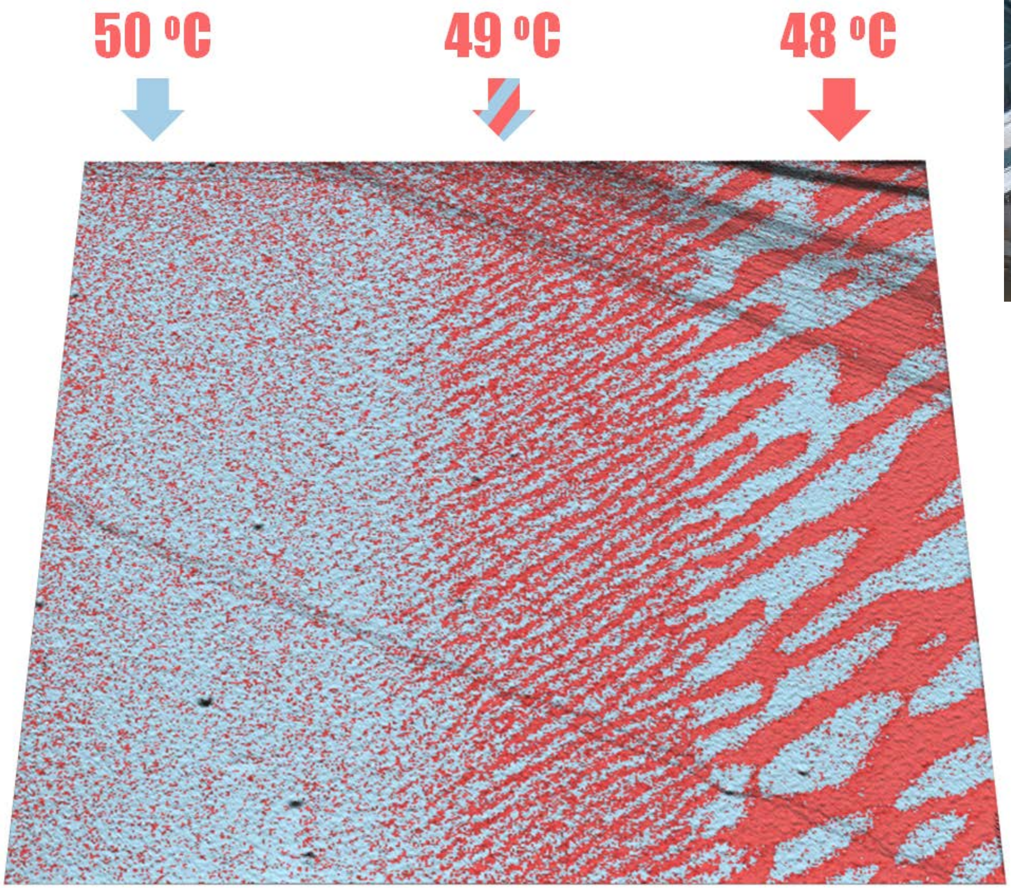
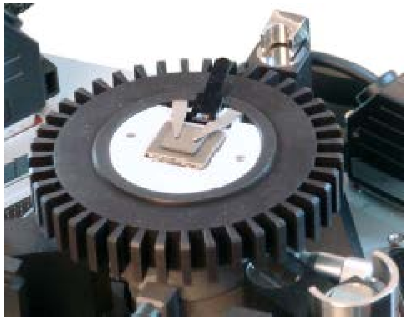
[1] A. Kalinin, V. Atepalikhin, O. Pakhomov, A. Kholkin, A. Tselev. An Atomic Force Microscopy Mode for Nondestructive Electromechanical Studies and its Application to Diphenylalanine Peptide Nanotubes. To be published in Ultramicroscopy

HybriD Piezoresponse Force Microscopy

Continuous PFM studies under varying temperature

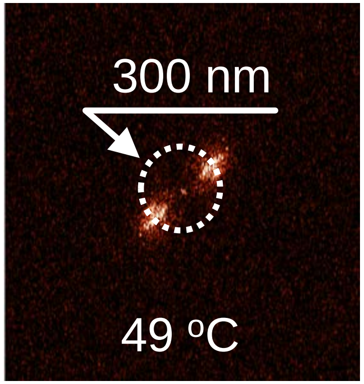


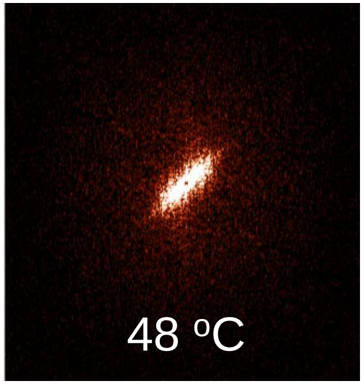


RT 300 °C

-30 120 °C

NT-MDT S.I. accessories for sample temperature control





In-situ HD PFM study of second-order phase transition of triglycine sulfate crystal. Scan size 15 15 µm. Sample courtesy: Dr. R. Gainutdinov, IC RAS

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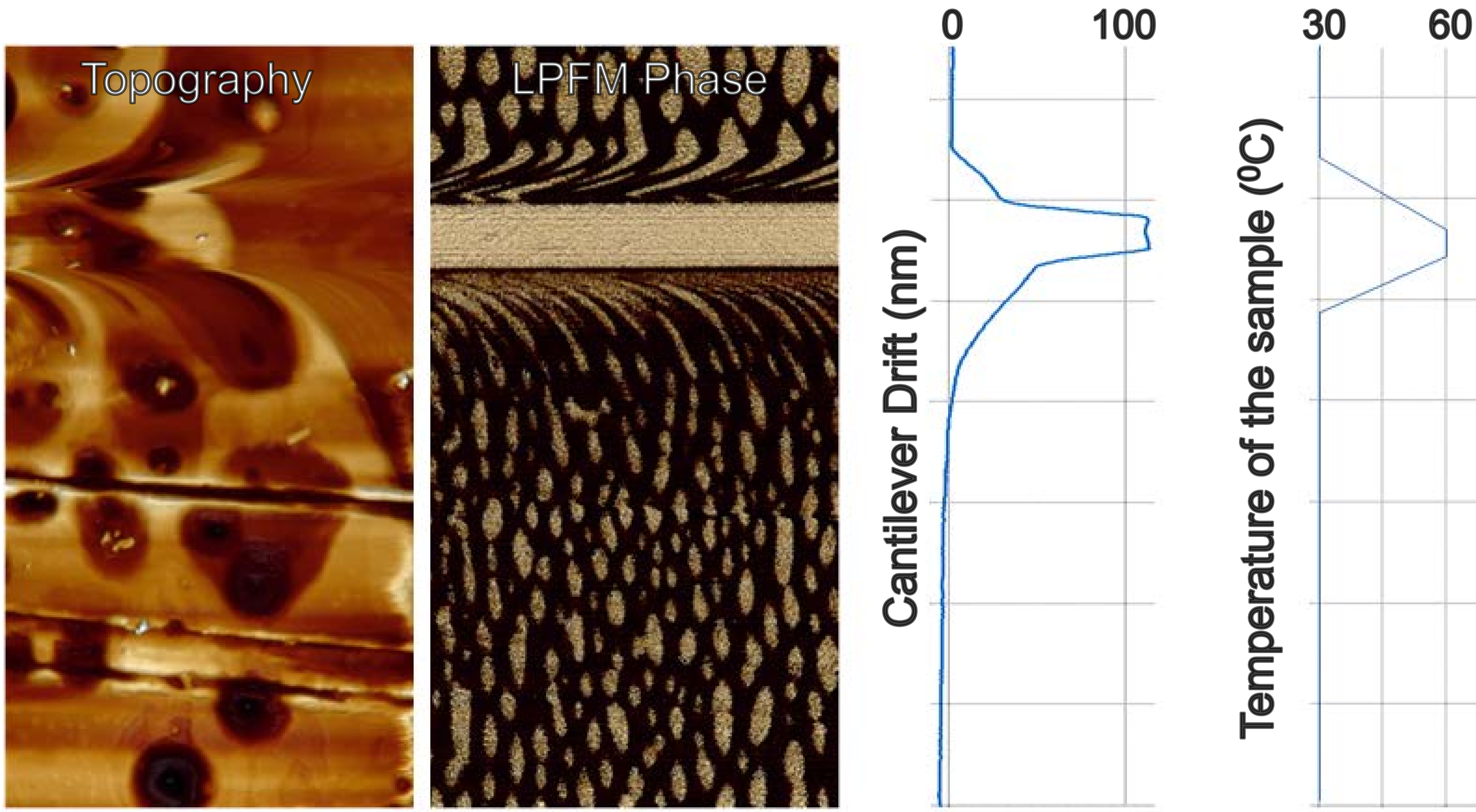
HybriD Piezoresponse Force Microscopy

Continuous PFM studies under variable temperature

>0.1 ºC/sec temperature change



In-situ HD PFM study of second-order phase transition of triglycine sulfate crystal. Scan size 15 15 µm. Sample courtesy: Dr. R. Gainutdinov, IC RAS

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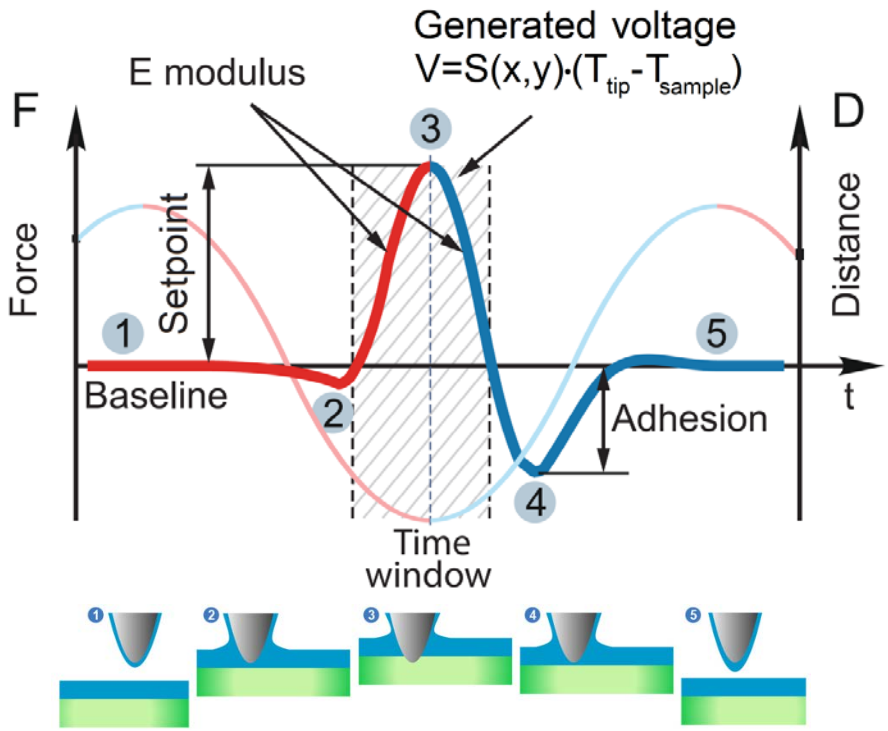
HybriD Scanning Thermoelectric Microscopy

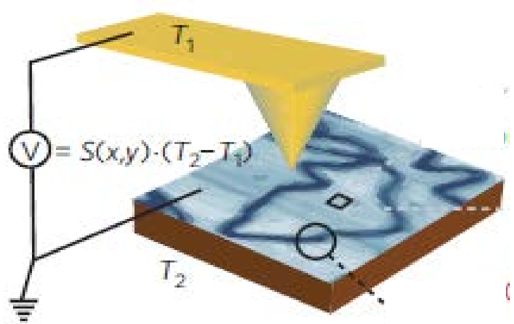
HybriD Scanning Thermoelectric Microscopy

HD SThEM working principle is based on direct measurement of generated voltage when conductive tip and sample under different temperatures contact each other (Seebeck effect) during fast force spectroscopy measurements



HD SThEM working principle

NT-MDT S.I. insert for SThEM measurement



S. Cho et al “Thermoelectric imaging of structural disorder in epitaxial graphene” Nature Materials, 2013.

J.C. Walrath *et al*, Quantifying the local Seebeck coefficient with scanning thermoelectric microscopy, Appl. Phys. Lett. 103 (2013) 212101.

HybriD Scanning Thermoelectric Microscopy

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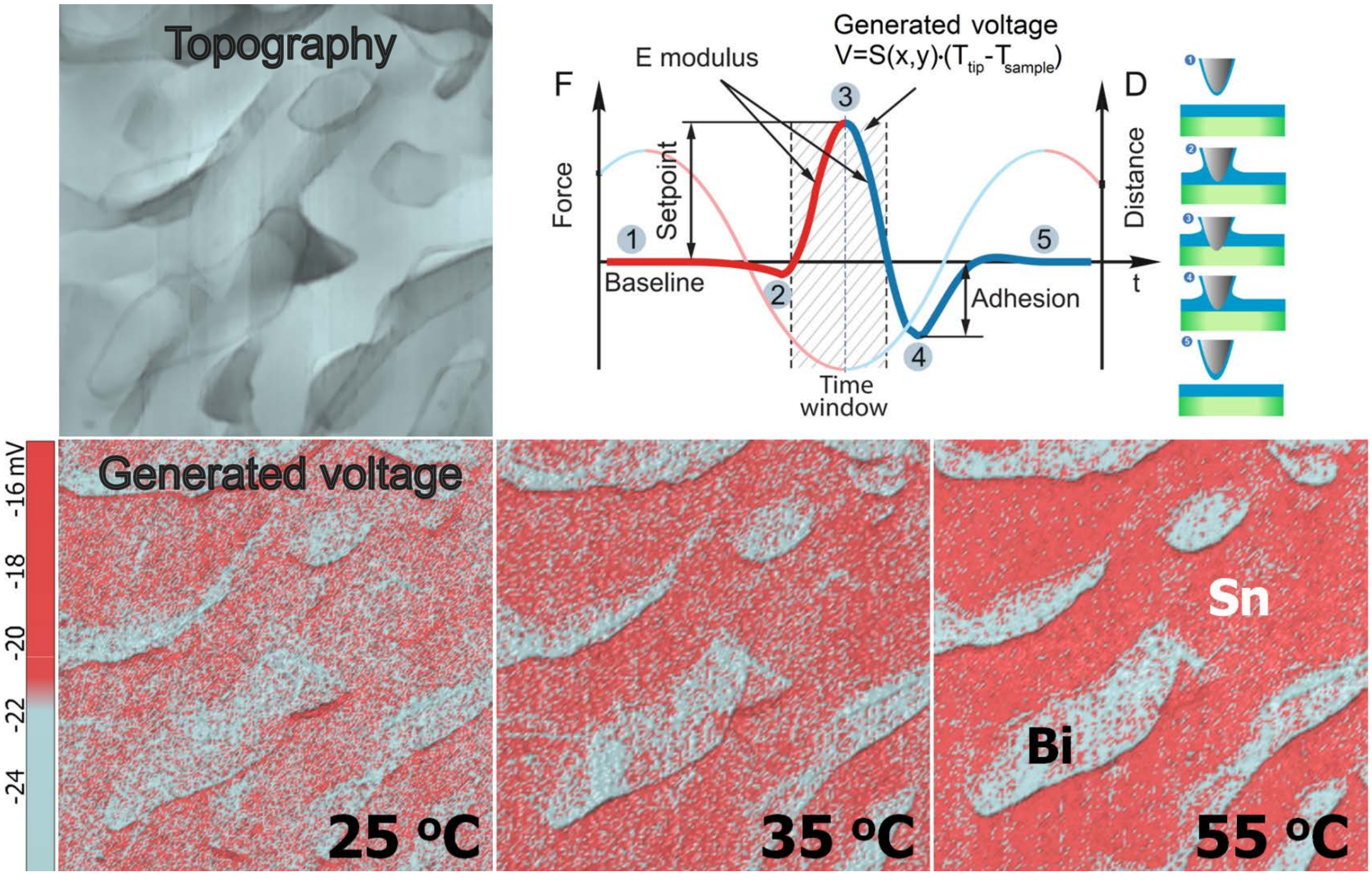


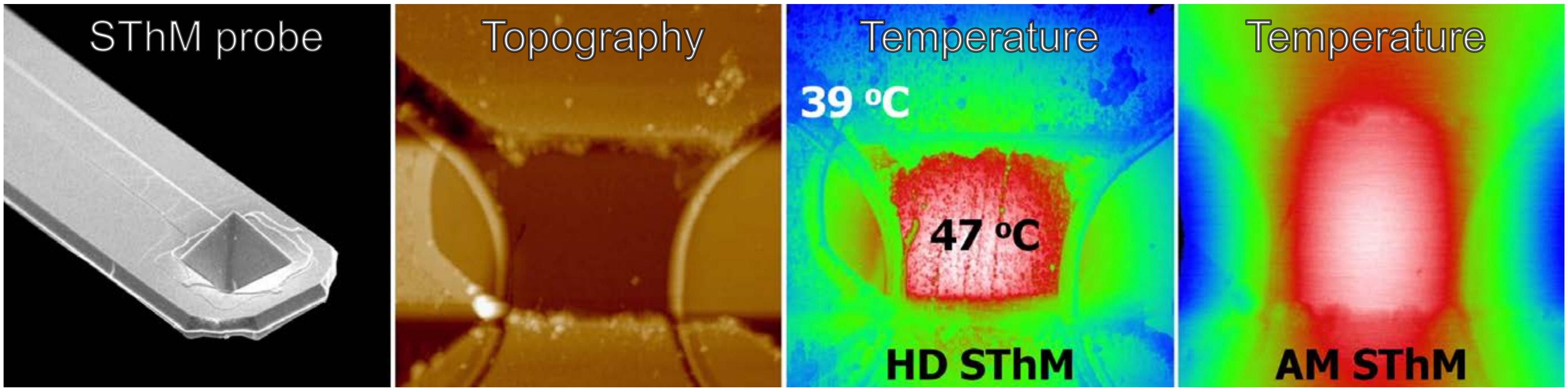
HD SThEM study of Tin-Bismuth alloy. Seebeck coefficient, S: Bi -72 mV/C, Sn -1.5 mV/C.

Scan size: 7 7 µm.

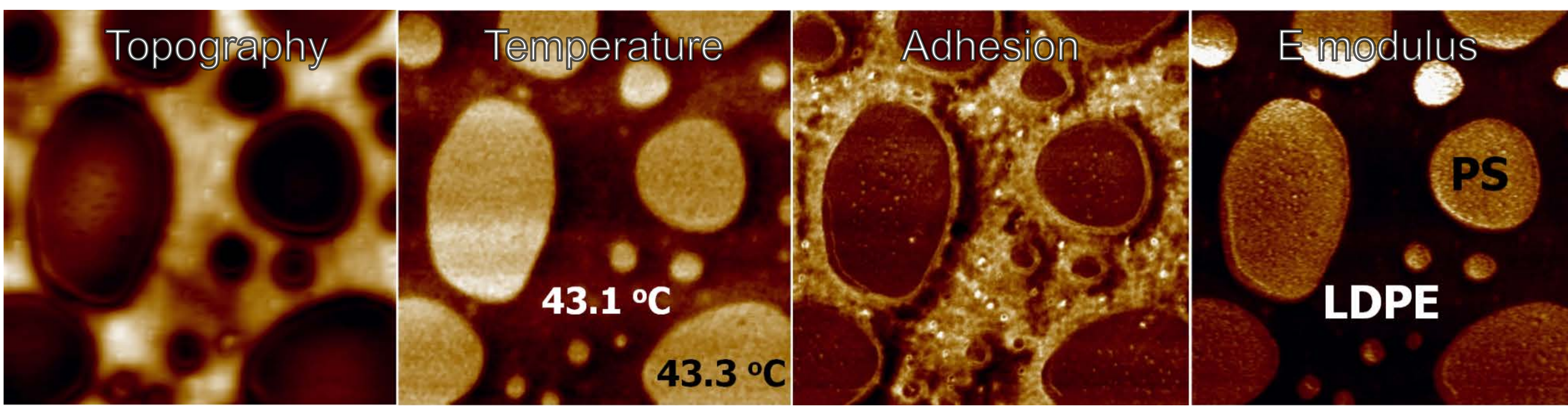
HybriD Scanning Thermal Microscopy (HD SThM)

HybriD Scanning Thermal Microscopy

HD Scanning Thermal Microscopy (HD SThM) allows studying local thermal properties – temperature and thermal conductivity – simultaneously with QNM measurements.



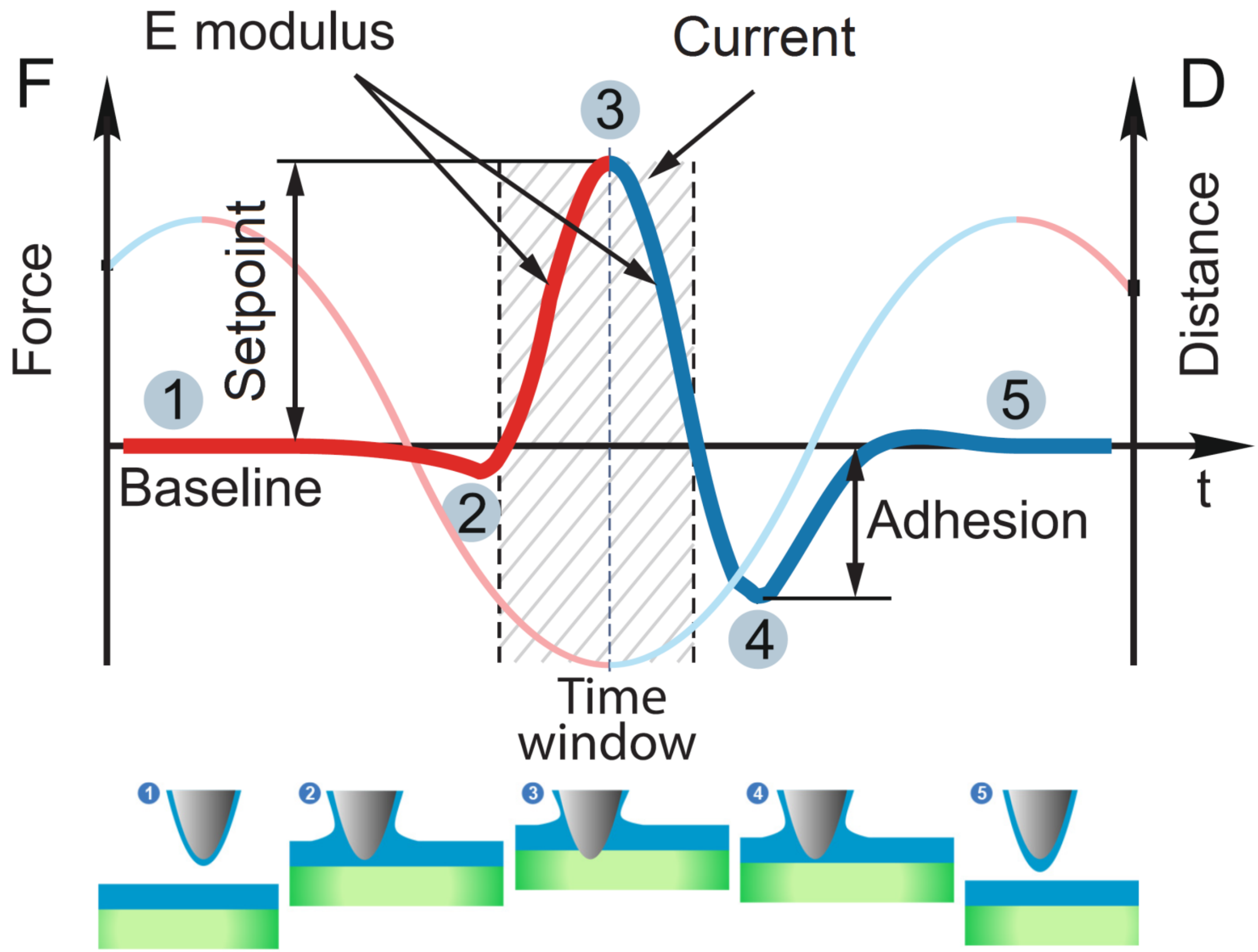
SEM image of AppNano VertiSense™ thermocouple probe and comparison of HD SThM and AM SThM techniques. Scan size: 17 17 µm.



HD SThM study of PS-LDPE. Scan size: 10 10 µm.

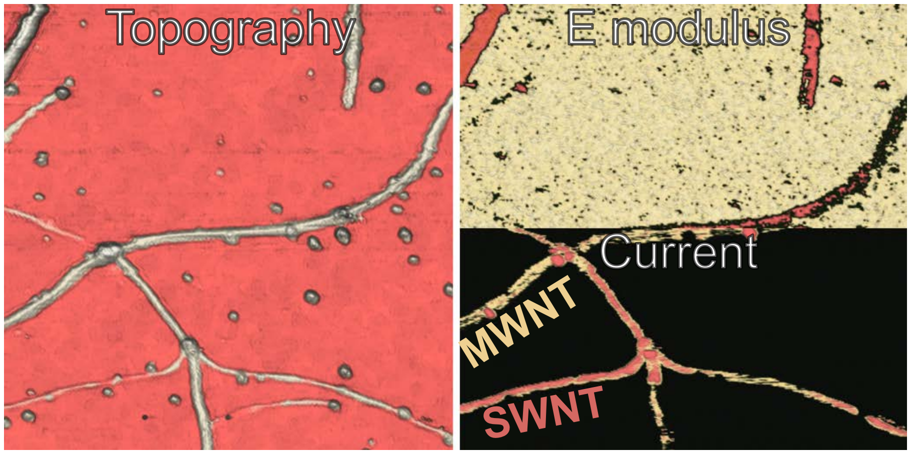
HybriD Conductive-AFM

Conductivity mapping while fast force spectroscopy measurements



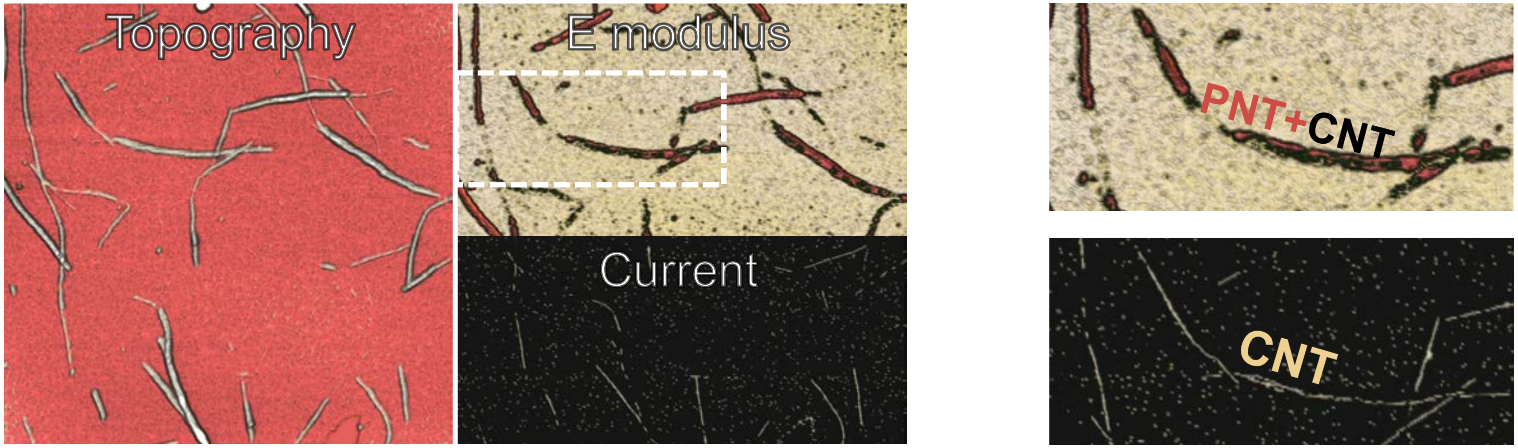
HybriD Conductive AFM

HybriD Mode drastically decreases the impact of lateral forces and simplifies C-AFM experiments



HD C-AFM study of carbon Nanotubes on Silicon.

Scan size: 1 1 µm.

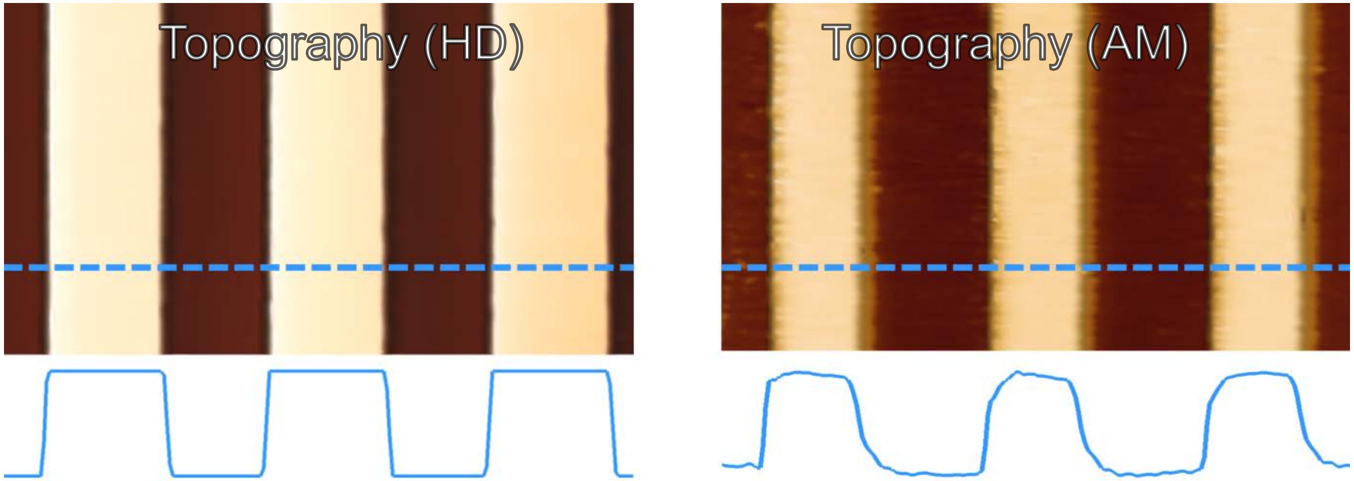


HD C-AFM study of coupled carbon and peptide Nanotubes. Sample courtesy: Dr. J. Montenegro, University Santiago de Compostela. Scan size: 3 3 µm[1].

[1] J. Montenegro, C. Vázquez-Vázquez, A. Kalinin, K.E. Geckeler, J.R. Granja, Coupling of carbon and peptide nanotubes, J. Am. Chem. Soc. 136 (2014) 2484–2491

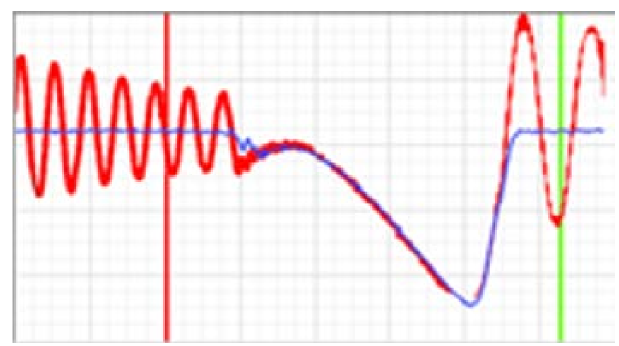
Advanced environmental studies:
Vacuum HD, Bio HD

Vacuum HD measurements



Topography of TGZ2 calibration grating measured in vacuum with use of HD and AM modes. Scanning speed is 1Hz. Grating period is 3 µm, height is 100 nm.

Vacuum AFM NTEGRA Aura



Example of filter operation.
Red – before, blue – after filter is appliedd

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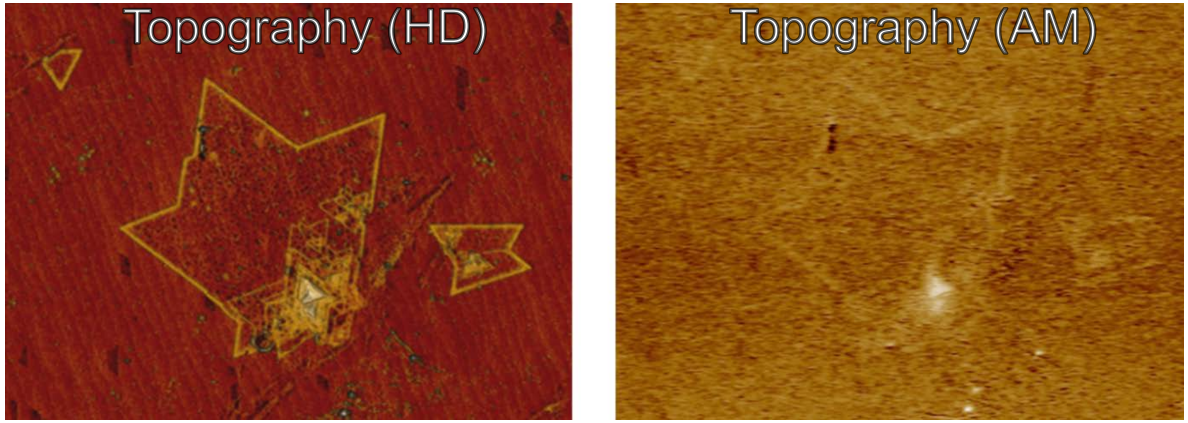
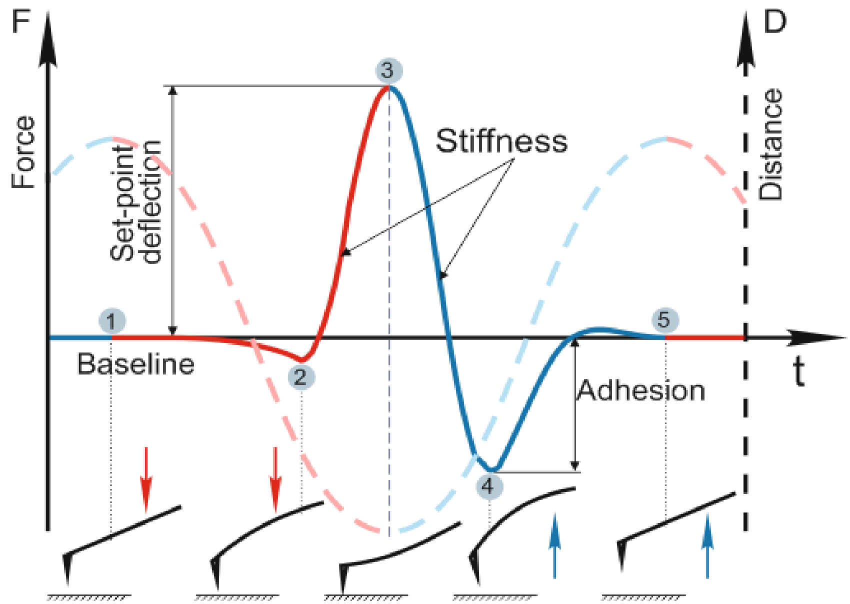
Vacuum HD measurements



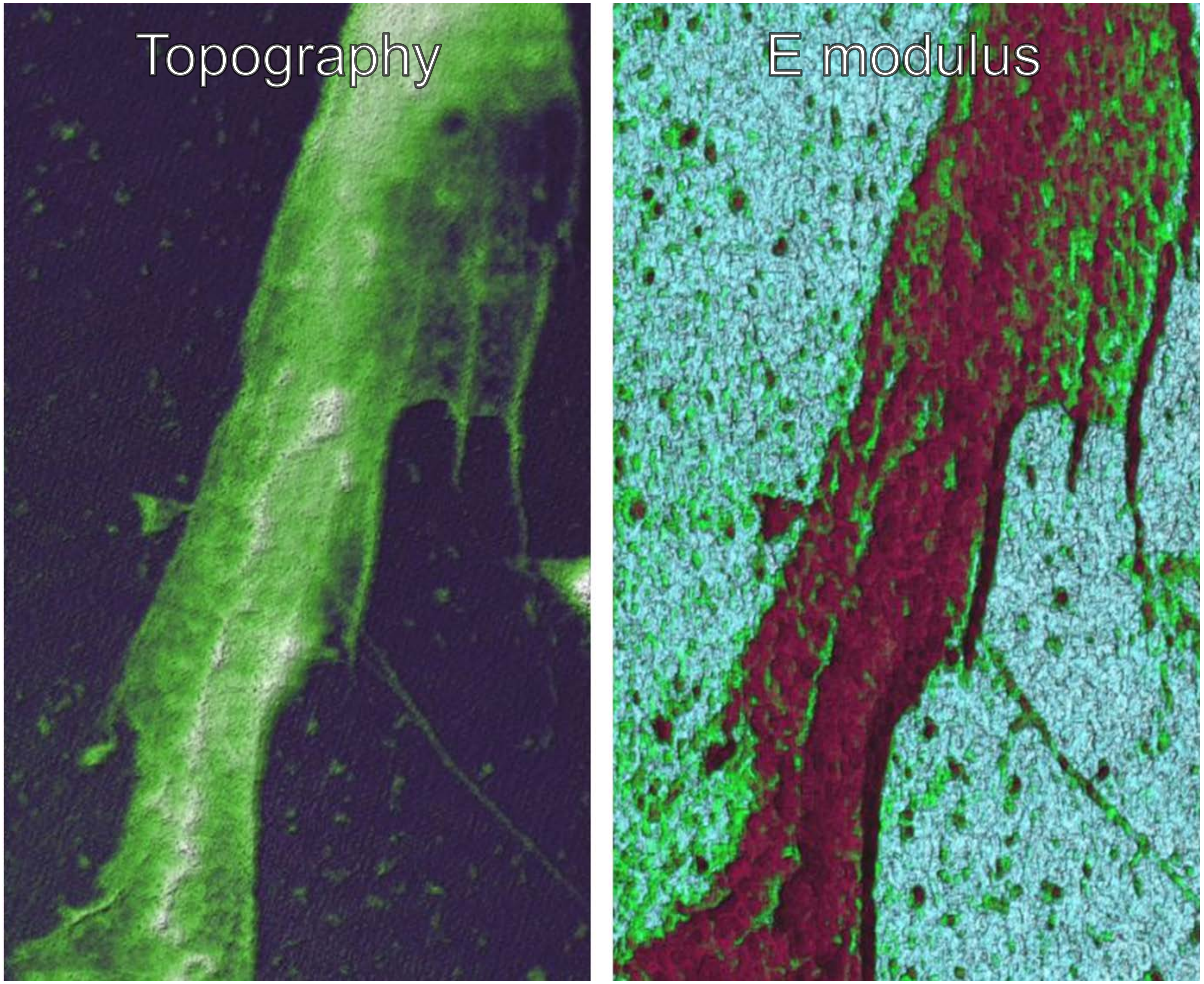
WS_2 monolayers grown on epitaxial graphene measured in vacuum with use of HD and AM modes. The influence of electrostatic forces is demonstrated. Scan size: 14 14 µm

Vacuum AFM NTEGRA Aura



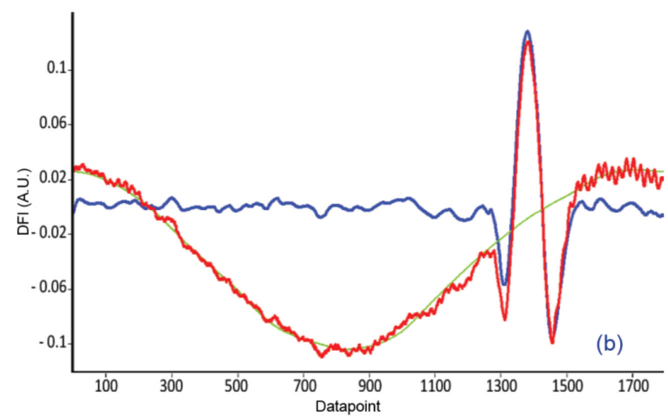
Set-point calculation principle eliminating electrostatic force gradient

Liquid HD measurements



Bio HD study of Stem Cell fragment in Liquid. Elastic Modulus range: 0.2-1.5 kPa. Scan size: 18 30 µm

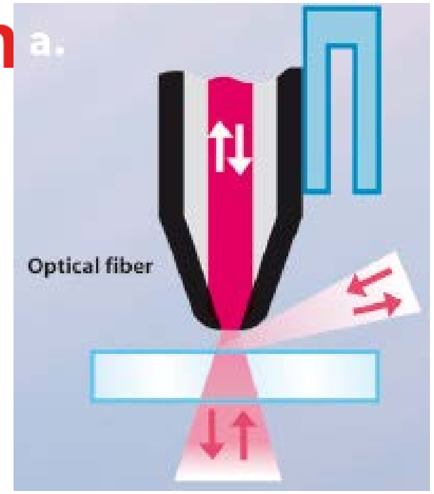
NT-MDT S.I. accessories for liquid measurements

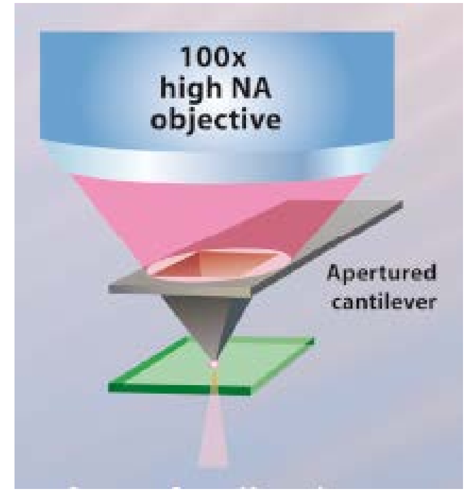


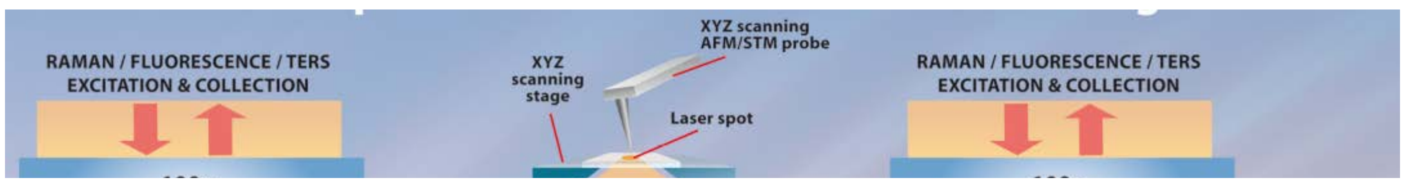
Example of filter operation

Advanced combined AFM-Optical modes

Optical Integration

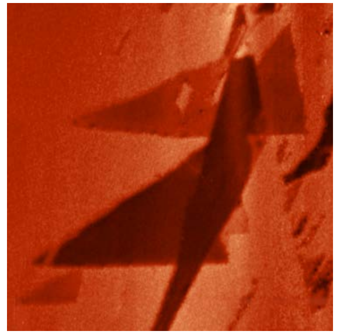






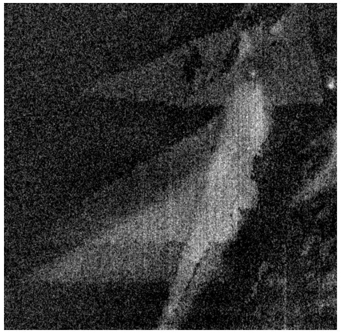
Graphene, AFM + Confocal Raman
One experiment - multiple data

Lateral Force Microscopy

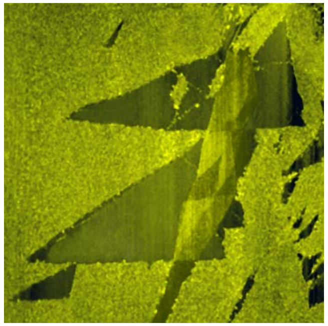


Electrostatic Force Microscopy

Force Modulation Microscopy

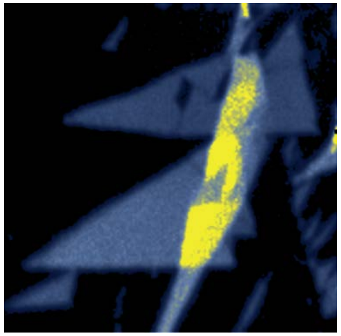


Capacitance Microscopy

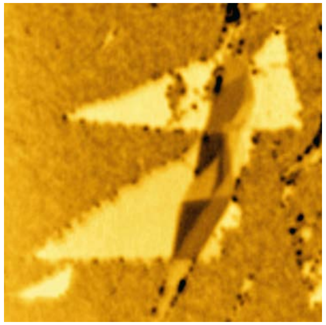


AFM Topography Size: 30*30 µm

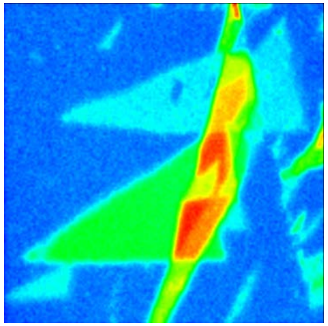
Scanning Kelvin Probe Microscopy



Raman Map, Mass Center of 2D (G’) Band



Confocal Rayleigh Microscopy

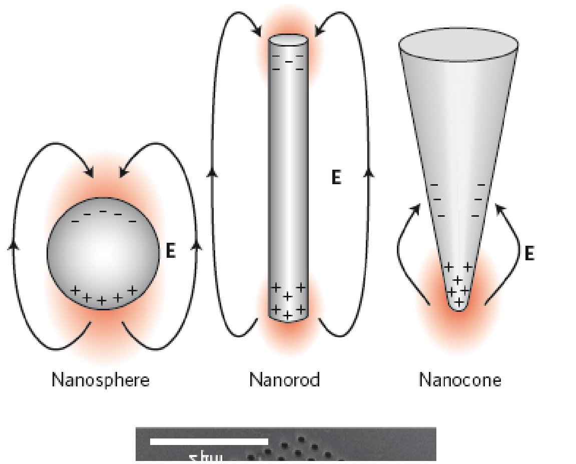


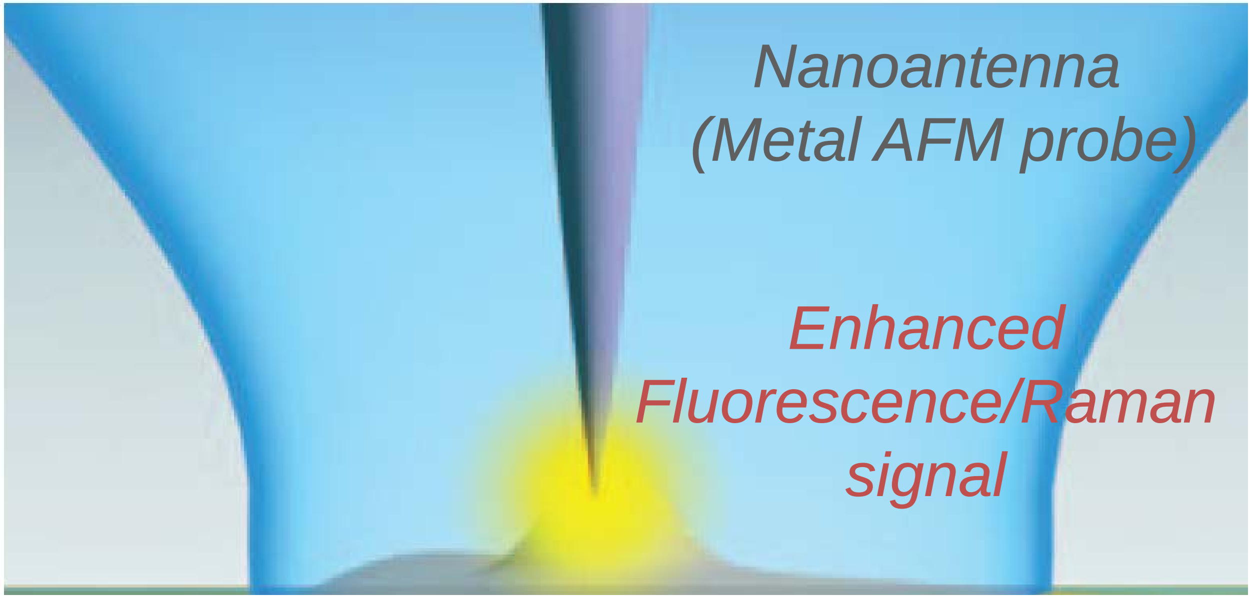
Raman Map, G-band Intensity

Tip Enhanced Raman Scattering (TERS) “Nano-Raman” imaging

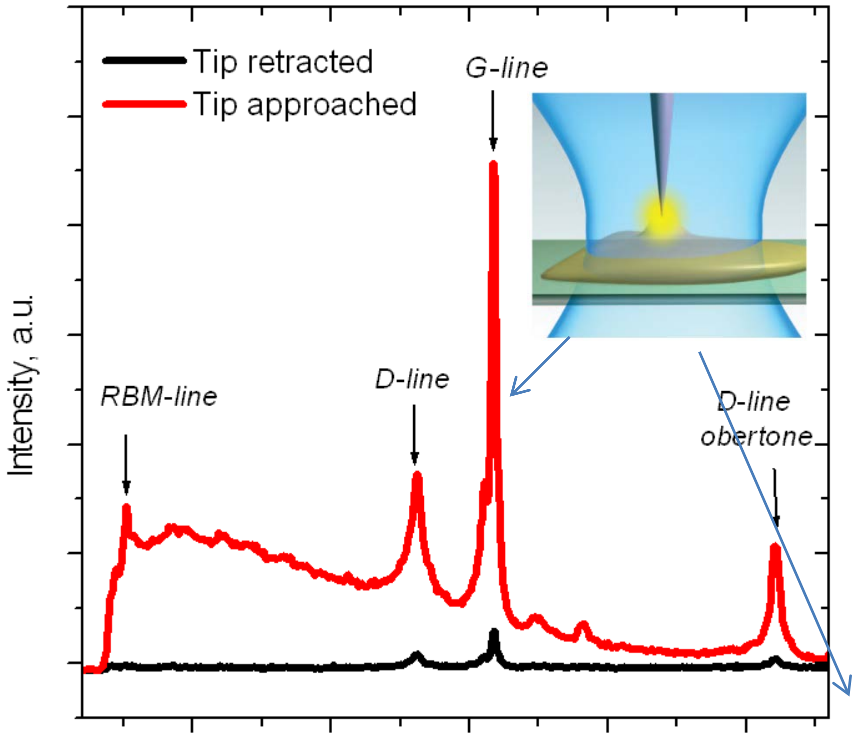
Raman/Fluorescence microscopy with subwavelength spatial resolution

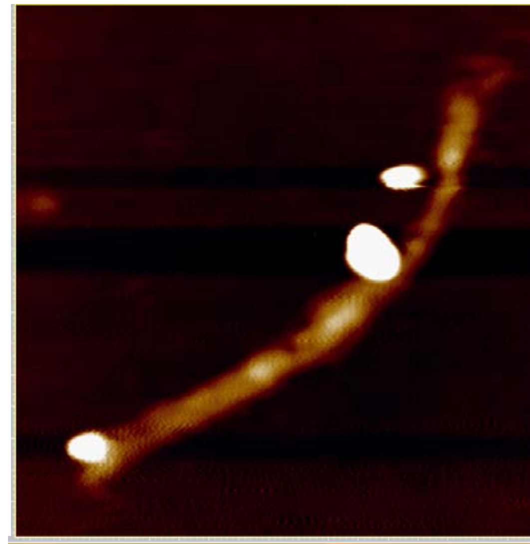
From S. Kawata et al., Nature Photonics (2010)



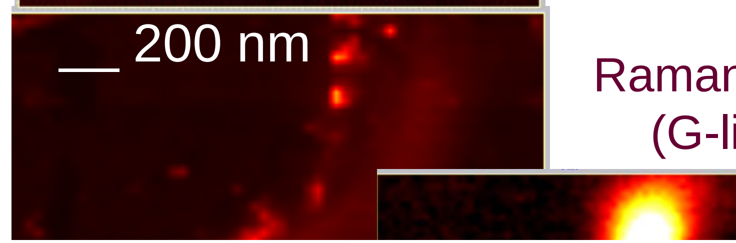


TERS imaging of single-walled CNT bundle



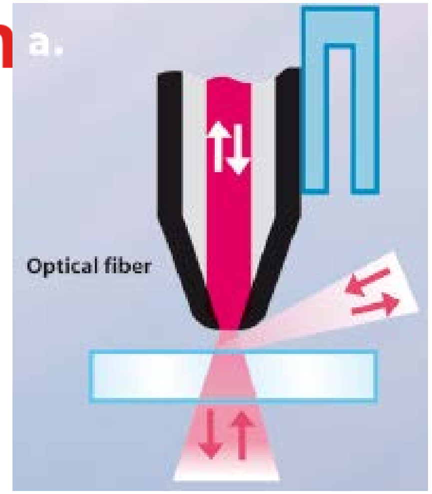


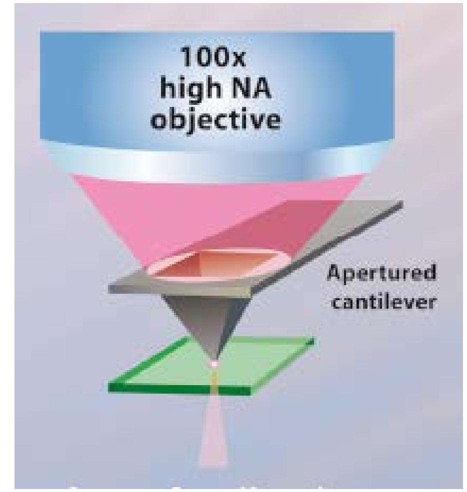
AFM topography
(height ~ 5 nm)

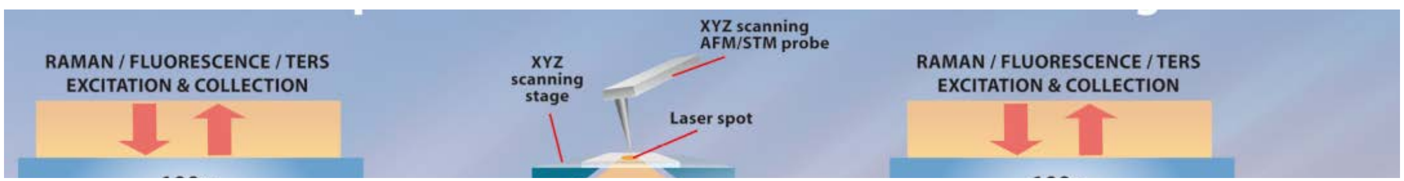


Raman map
(G-line)

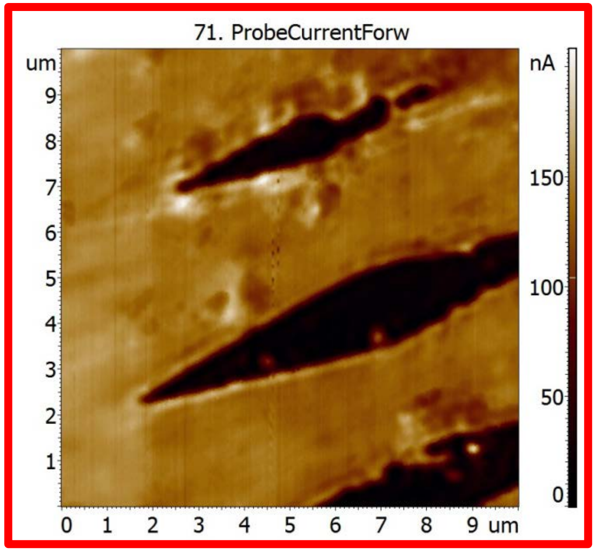
Optical Integration



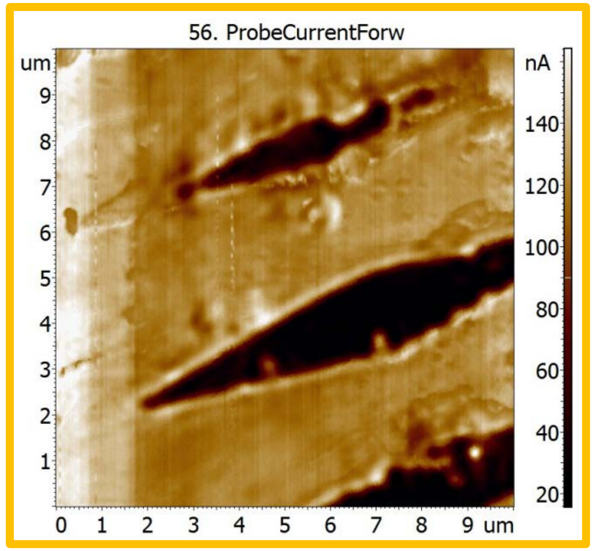




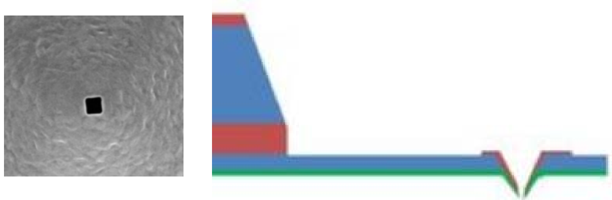
HybriD Scanning Near-field Microscopy



SNOM in contact

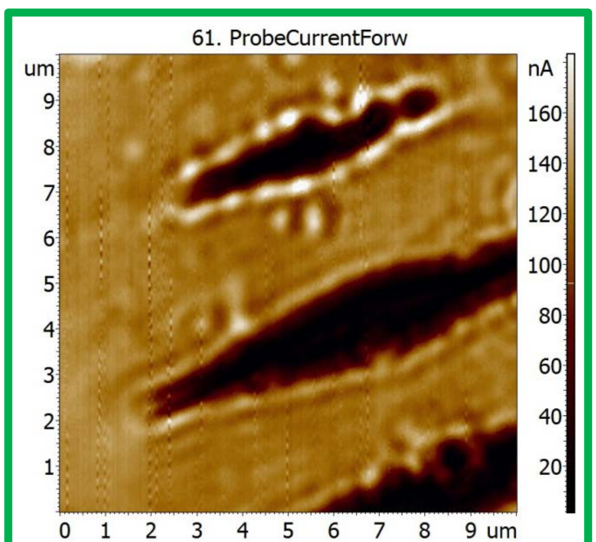


SNOM at 100 nm from surface

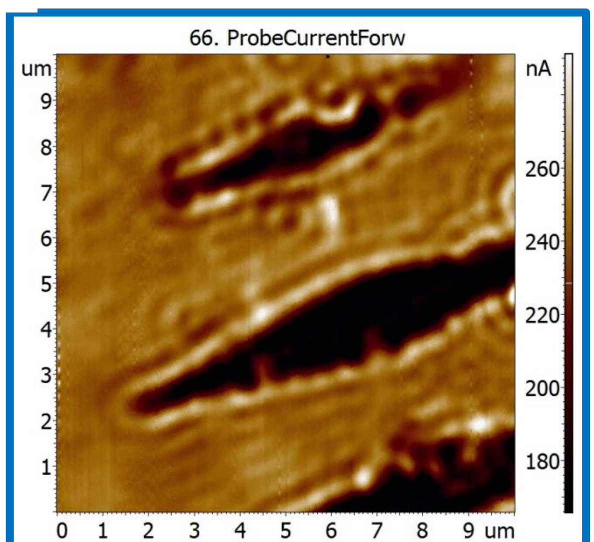


Aperture AFM SNOM probe

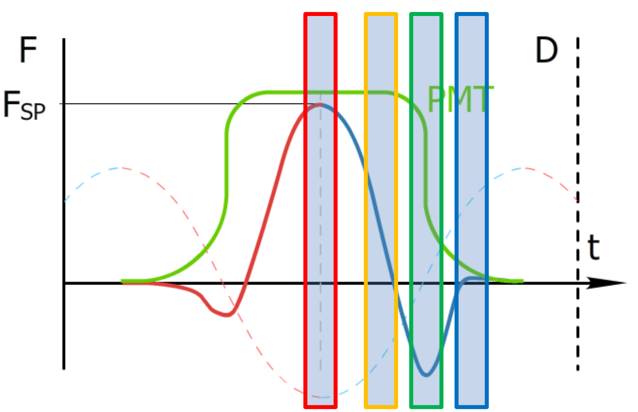
PMT signal per one cycle



SNOM at 220 nm from surface



SNOM at 290 nm from surface



Schematic force curve and optical curve

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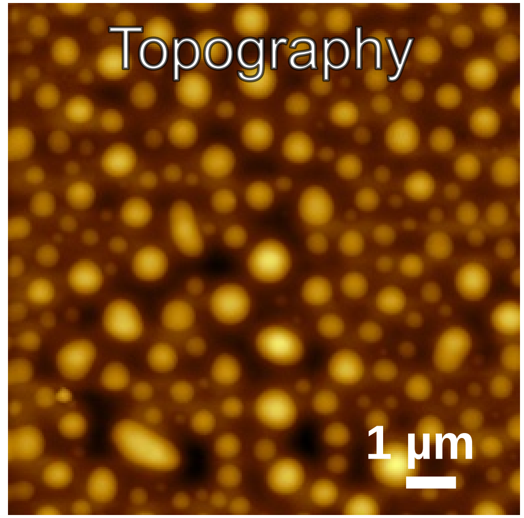
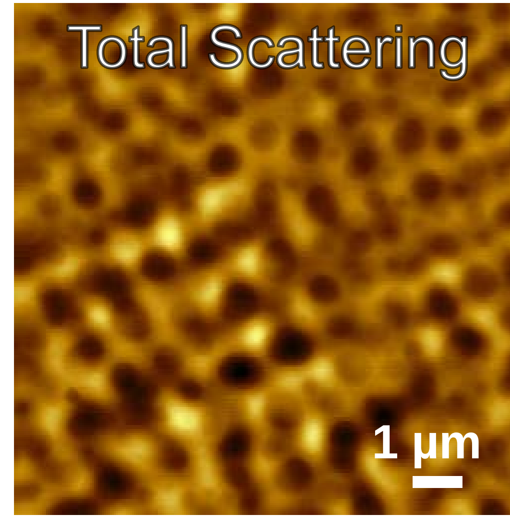
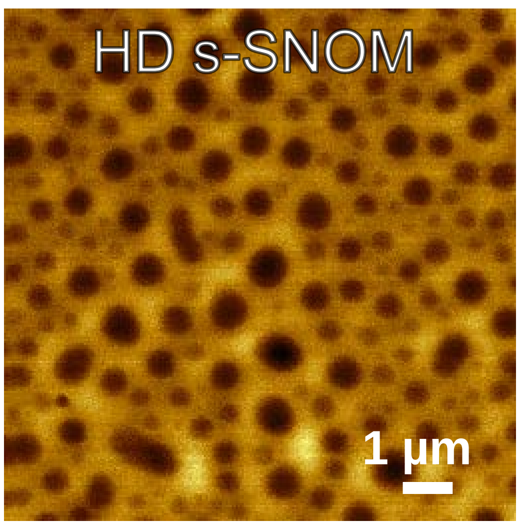
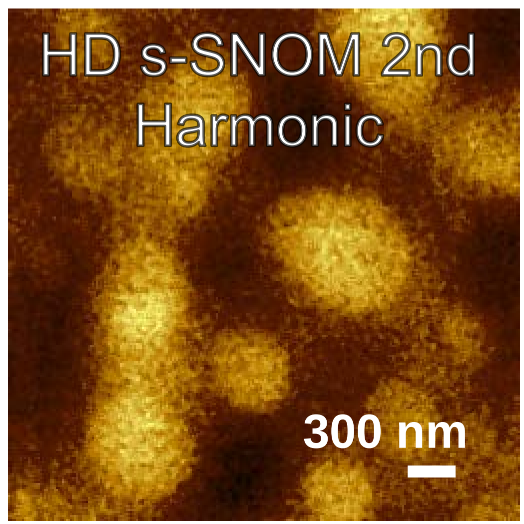
HybriD Scattering Scanning Near-field Microscopy

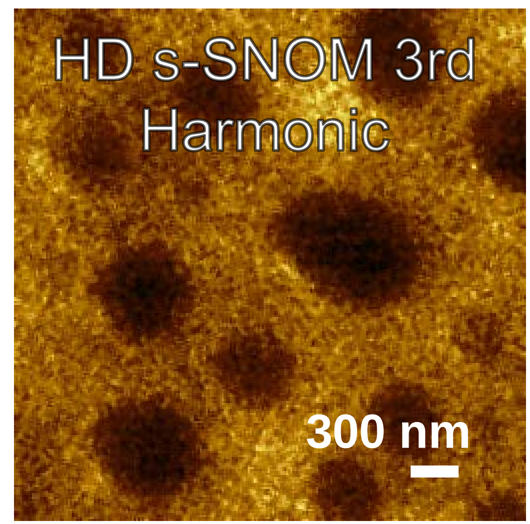
PMT signal per one cycle – “optical curve”





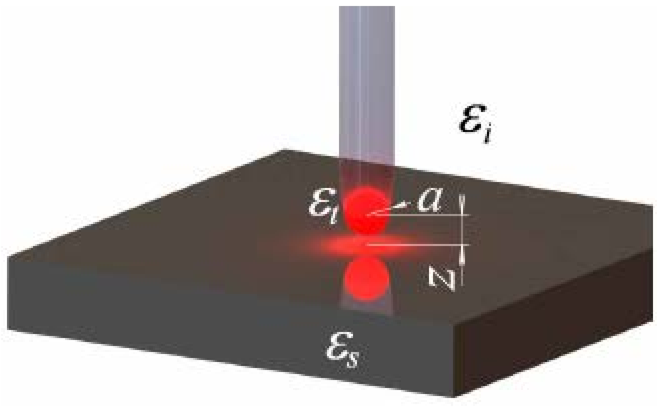




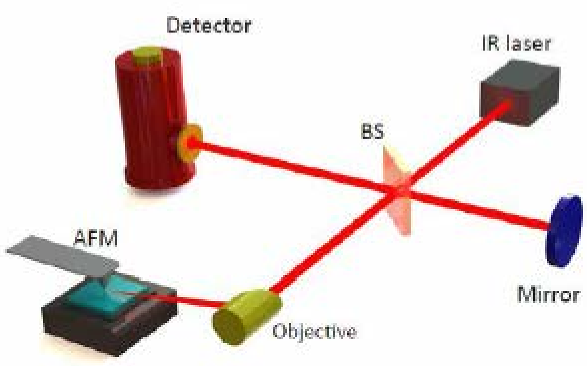


HD s-SNOM study of PS/PBD film demonstaring better than 100 nm optical resolution

IR Microscopy and Spectroscopy



AFM tip interacting a sample



IR s-SNOM measurement scheme

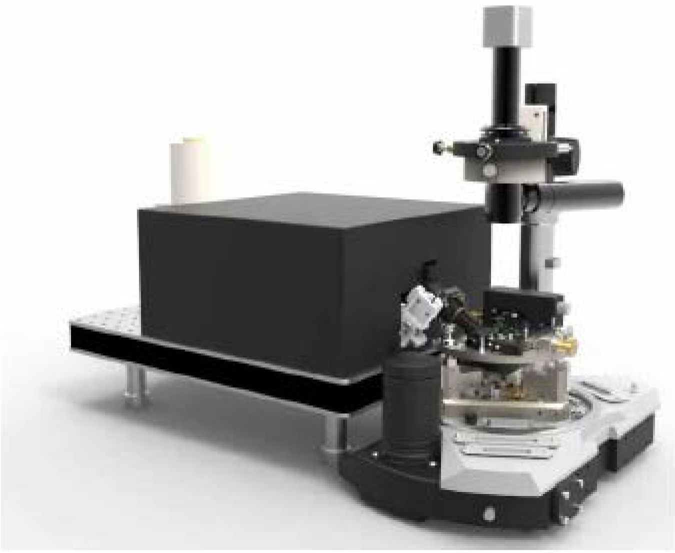
$$E_{scatt} \approx E_{loc}\alpha_{eff}$$

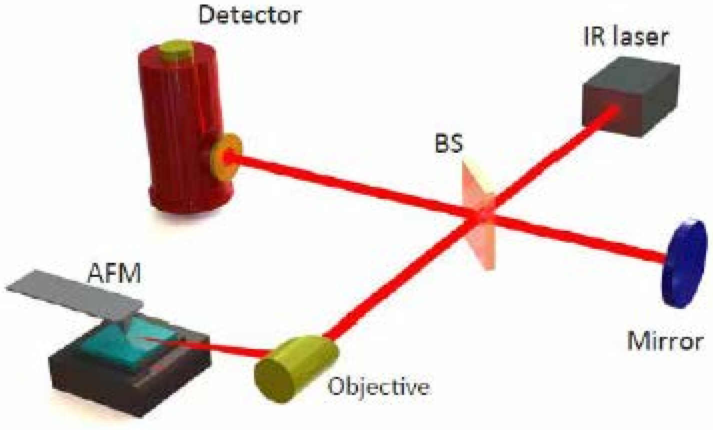
$$\alpha_{eff} = \frac{\alpha(1-\beta)}{1-\dfrac{\alpha\beta}{32\pi(z+a)^3}}$$

$$\beta = \frac{\varepsilon_s - 1}{\varepsilon_s + 1}$$

$$\alpha = 4\pi a^3 \frac{\varepsilon_t - \varepsilon_i}{\varepsilon_t + 2\varepsilon_i}$$

IR Microscopy and Spectroscopy



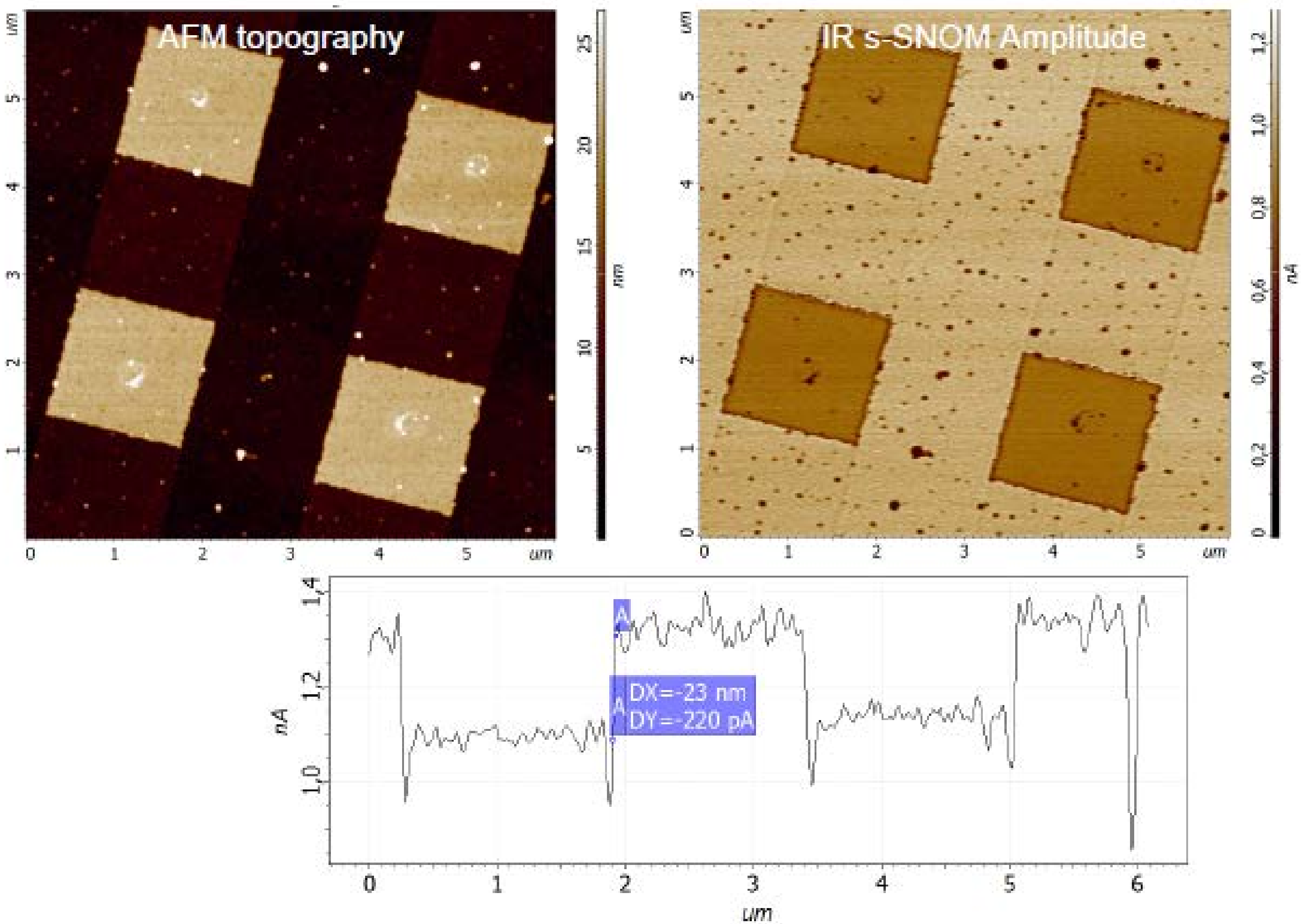


NTEGRA IR principal scheme

- IR s-SNOM microscopy and spectroscopy with 10 nm spatial resolution
- Wide spectral range of operation: 3-12 µm
- Incredibly low thermal drift and high signal stability
- Versatile AFM with advanced modes: SRI (conductivity), KPFM (surface potential), SCM (capacitance), MFM (magnetic properties), PFM (piezoelectric forces)
- HybriD Mode^{TM} - quantitative nanomechanical mapping
- Integration with microRaman (optional)

NT-MDT Spectrum Instruments

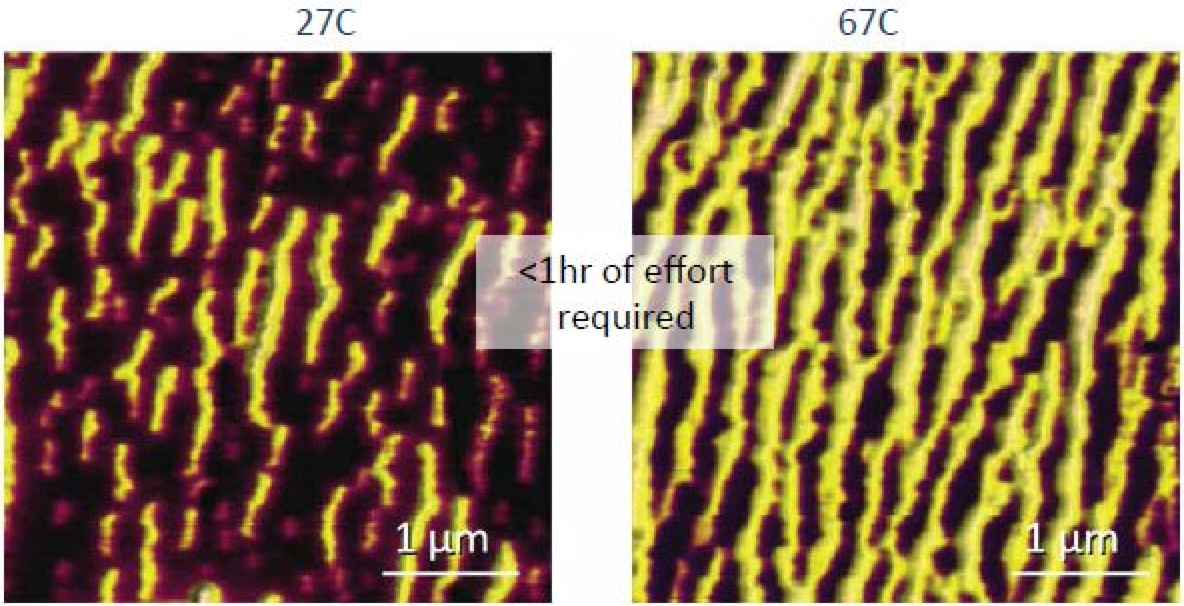
IR Microscopy and Spectroscopy



Si/SiO$_2$ calibration grating (TGQ).
Scan size 6×6 um.

IR Microscopy and Spectroscopy VO2

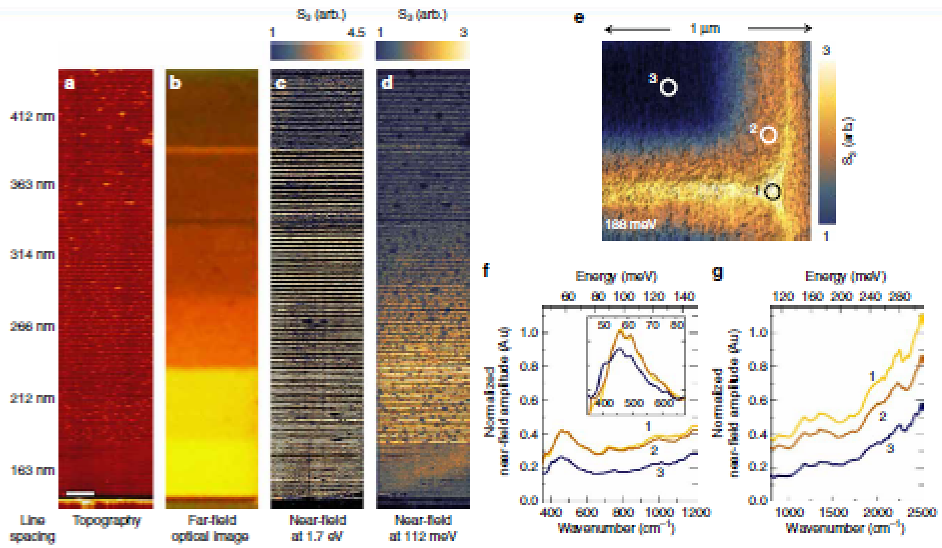
IR s-SNOM Reflection



- Superior high temperature performance: under 1 hour needed to acquire images 40C apart. Compare to days on competitor's system
- Low drift and high signal stability: <1um XY drift from 27 to 67C, no realignment of nanoReflection optics needed

ample courtesy to prof. Liu (Stony Brook University, New York, USA)

IR s-SNOM: Dual-band heavy fermion materials investigation (SmS)



IR and visible near-field characterization of SmS metamaterials created via AFM lithography.

(a) The topography of a color gradient MM with decreasing spacing between the patterned lines (listed on the left) is shown for a depth of ~12 nm. The scale bar is 500 nm.

(b) A far-field optical image of the same gradient MM; the color change from red to golden is achieved by altering the lithographic line spacing.

(c) Room-temperature near-field image collected at 1.7 eV

(d) Room-temperature near-field image collected at 112 meV. The near-field 3rd harmonic amplitude is shown in false-color, where blue indicates regions of semiconducting conductivity and gold indicates regions of metallic conductivity.

(e) The near-field amplitude at 188 meV (1515 cm^{-1}) and 295K is shown in false color for a 1 μm^2 region of a grating pattern. The near-field amplitude change of the patterned area (in gold) is normalized to the semiconducting response (in blue). Three locations are marked in the image, indicating golden IV (1), transition (2), and semiconducting (3) regions of the MM.

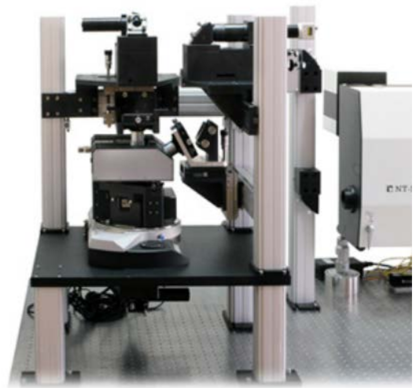
(f) Broadband near-field spectroscopy (normalized to a gold thin film) at 295 K for the locations specified in the 1 μm^2 image, indicating the presence of the localized golden IV phase on the surface of the SmS.

Stephanie N. Gilbert Corder et. al., Near-field spectroscopic investigation of dual-band heavy fermion materials, Nature Communications, 8:2262, 2017

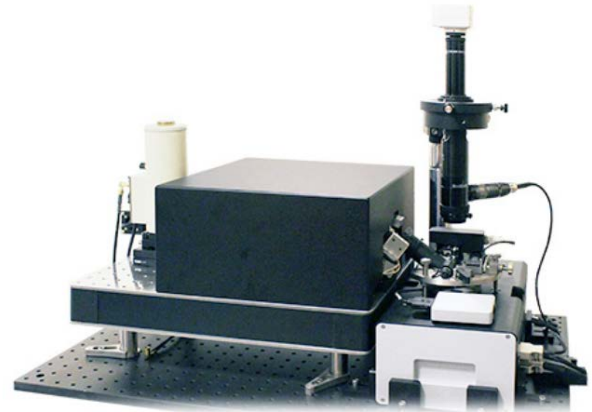
Conclusion

HybriD mode and HD 2.0 Control Electronics are compatible with all the product line of NT-MDT Spectrum Instruments

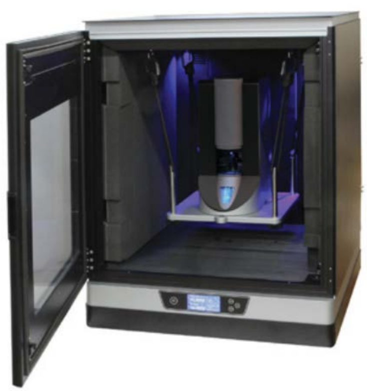
Modular SPM NTEGRA



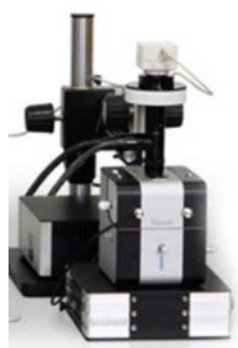
Automated AFM-Raman, SNOM and TERS system NTEGRA SPECRTA II



AFM-IR & sSNOM system NTEGRA Nano IR



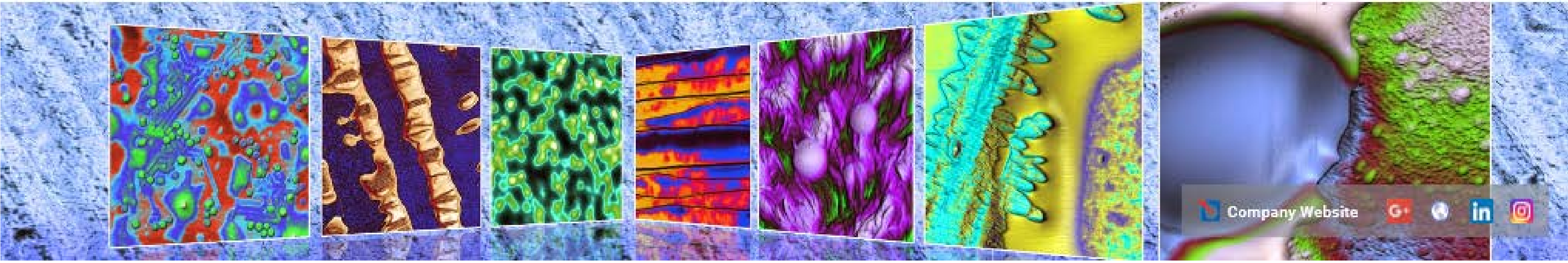
Ultra-low-drift automated SPM Titanium



Practical AFM Solver NANO

Automated SPM NEXT

Automated large-sample AFM VEGA



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